Anal. Calcd. for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31; N, 5.45; neut. equiv., 257. Found: C, 65.25; H, 4.30; N, 5.27; neut. equiv., 254.

Quantitative hydrogenation of 479 mg. (18.6 mmoles) of the diene in ethyl acetate solution was carried out over palladium-on-charcoal until 1 equiv. of hydrogen had been taken up. The solvent was evaporated at reduced pressure until the volume of solution remaining was 8 ml. This solution was allowed to stand at −5° overnight. In this manner was obtained 230 mg. of straw-colored crystals, m.p. 176–178°. This material and an additional 150 mg. of material obtained as a second crop were chromatographed on a silica gel column. Elution was carried out using 80 ml. of carbon tetrachloride, 50 ml. of 25% chloroform–75% carbon tetrachloride, 50 ml. of 50% chloroform–50% carbon tetrachloride, 50 ml. of chloroform, 50 ml. of 50% ether–50% chloroform. No bands came off the column until the last solvent system was used. The material obtained, 301 mg., was recrystallized from carbon tetrachloride giving 3-(*o*-nitrophenyl)-norbornene-2-carboxylic acid, m.p. 176–177.5°. The infrared spectrum (carbon tetrachloride) showed a band at 5.96 μ but no bands at 6.35 and 14.2 μ.

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.85; H, 5.05; N, 5.40; neut. equiv., 259. Found: C, 64.95; H, 5.20; N, 5.35; neut. equiv., 258.

Spectroscopic Studies.—Ultraviolet absorption data were determined with a Cary recording spectrophotometer, Model 15, employing 95% ethanol as a solvent. The *trans*-cinnamic acids used in these studies were purchased or prepared according to well-known methods described in the literature. Infrared spectra were determined with a Baird infrared spectrophotometer using carbon tetrachloride and chloroform solutions and in some cases potassium bromide pellets. The n.m.r. spectra were obtained from a Varian Model A-60 employing deuterated chloroform as the solvent and tetramethylsilane as an internal standard. Concentrations of 10% (w./v.) were employed throughout and more dilute solution spectra (5%) were also measured in the case of **3**, **3**-H_2, **8**, and **8**-H_2. There was no observable dilution effect on the τ-values.

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Medium Effects, Isotope Rate Factors, and the Mechanism of the Reaction of Diphenyldiazomethane with Carboxylic Acids in the Solvents Ethanol and Toluene[1]

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It is proposed that the mechanism of the reaction of molecular acids (HA) with diphenyldiazomethane (DDM) in ethanol involves a slow proton transfer to give the ion pair $(C_6H_5)_2CHN_2{}^+A^-$. This is followed by the expulsion of nitrogen to give a second ion pair $(C_6H_5)_2CH^+A^-$ which may then either collapse to form ester or dissociate to form benzhydryl ethyl ether. This mechanism is consistent with the second-order kinetics, isotope effect $k_H/k_D = 3.5$ (benzoic-*h* acid in ethanol-*h* and benzoic-*d* acid in ethanol-*d*), and with an amount of ester in the product ($\alpha = 0.60$–0.70) which is essentially independent of the molecular acid or of deuterium substitution in it. Two factors, the polarity of the medium and the presence of more reactive acid dimers, account for medium effects on the slow step of the reaction of DDM with monomeric carboxylic acids. Thus, the second-order rate constant increases by a factor of 1.5 as the concentration of benzoic acid increases (0.0–0.7 *M*); addition of toluene causes the rate constant to drop from 0.69 (ethanol) to 0.42 (85 vol. % toluene) and then rise to 0.73 l. mole^{-1} min.$^{-1}$ (toluene) at 27°. In toluene, the apparent second-order rate constant increases with benzoic-*h* and decreases with benzoic-*d* acid concentrations resulting in the peculiar divergence $k_H/k_D = 1.8$–3.7 (acid 0.015–0.25 *M*). It is believed that in toluene it is the dimer which is the reacting acid species and the relatively large concentration dependence is ascribed to a medium effect rather than to changes in acid association. Concerning the product-partitioning steps, it is believed that they are rapid and unselective or essentially diffusion controlled. However, specific "chemical factors," *i.e.*, the polarity of the medium, the nucleophilicity of the solvent, and the strength of added acids, compete with or alter the diffusion rates so that the ester to ether ratio in the products does change. The similarity to product-partitioning steps of solvolysis reactions is emphasized.

Certain reactions achieve a special importance. Next to p*K* values of acids, the rates of reaction of

$$RCOOH + (C_6H_5)_2CN_2 \xrightarrow{C_2H_5OH} (C_6H_5)_2CHOC_2H_5 + (C_6H_5)_2CHOOCR + N_2 \quad (1)$$

acids with diphenyldiazomethane (DDM) are perhaps the most convenient measure of the effect of a substituent on reactivity. Thus, the literature contains examples from diverse acid families, *e.g.*, benzoic,[2–6] phenylacetic,[7] phenylpropionic,[8] cinnamic,[9] phenylpropiolic,[10] 2-furoic,[11] ferrocenoic,[12] alkanoic,[13] 4-cyclohexylcarboxylic,[14,15] 4-bicyclo[2.2.2]octanecarboxylic,[16] etc.[17] Despite the extent of its application, aspects of the reaction mechanism remain unsettled.[18] In the course of the present work, we found significant medium effects as well as results that bear on the mechanism in both ethanol and toluene. These are two solvents in which much of the previous work has been carried

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[1] Acknowledgment is made to the U. S. Army Research Office, Durham, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 44T.

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[5] A. Buckley, N. B. Chapman, and J. Shorter, *ibid.*, 178 (1963).

[6] (a) K. Bowden, A. Buckley, N. B. Chapman, and J. Shorter, *ibid.*, 3380 (1964). (b) In addition to normal α-values in ethanol, these workers have established $\alpha = 0.69$–0.73 as the "normal" range in 2-methoxyethanol. In *t*-butyl alcohol and in three substituted benzyl alcohols the variation in α is larger so that the notion of a representative α is no longer useful; as *o*-chlorobenzoic acid leads to more ester than does *p*-chlorobenzoic acid, these workers suggest that secondary steric effect may be operative in these solvents.

[7] R. A. More O'Ferrall and S. I. Miller, *J. Am. Chem. Soc.*, **85**, 2440 (1963).

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[18] For a survey of the mechanisms of the reactions of aliphatic diazo compounds in general see H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, Chapter 6.

out and, presumably, they are representative of wider groups of hydroxylic and aprotic solvents. As our discussion will cover previous results as well as our own, it is recommended that the reader scan our tables of data before passing to the next section.

Results and Discussion

Mechanism in Ethanol.—Using both strong and weak acids, Roberts, *et al.*, observed that reaction 1 was first order in acid and first order in DDM.[19-23] With strong acids, benzhydryl ethyl ether was the sole product but with undissociated acids, a mixture containing both benzhydryl ether and ester was obtained. The dependence of the reaction rate on the concentration of molecular acids strongly suggested general acid catalysis. This result pointed to a rate-determining proton transfer, and the conclusion was supported by the difference in rates of protio and deuterio acids: k_H/k_D was *ca.* 3.5 for benzoic and acetic acids (Table II).[22,23]

Table I

The Fraction of Combined Acid in the Product of the Reaction[a]

$$(C_6H_5)_2CN_2 + HA \xrightarrow{C_2H_5OH} (C_6H_5)_2CHA + (C_6H_5)_2CHOC_2H_5$$

Acid	Temp., °C.	k, l. mole^{-1} min.$^{-1}$	α[a]
Benzoic-*h*[b]	30	1.04	0.63[c,d,e]
Benzoic-*d*	35.5	0.46	.66[c]
o-*t*-Butylbenzoic[b]	30	2.4	.70[e]
2,6-Dichlorobenzoic[b]	30	27.4	.69[f]
2-Furoic[b]	25.9	4.22	.57[g]
cis-1,4-Cyclohexanedicarboxylic acid monomethyl ester[b]	30	0.50	.64[h]
Formic	25.9	1.64	.81[c]
Acetic	25.9	0.42	.67[c,i,j]
Phenylacetic	26	0.83	.75[c,k]
2,4-Dinitrophenol	30	1.47	.66[l]
2,6-Dinitrophenol	25.9	7.8	.68[c]
2,4-Dinitronaphthol	25.9	8	.05–.4[c]
Picric	30	300[m]	0.0[m]
H^+ (*p*-toluenesulfonic)	30	330[m]	0.0[m]

[a] Ref. 26. α's from the literature have been adjusted by using our value[7] of 102 for the extinction coefficient of diphenyldiazomethane at 525 mμ. [b] One example of a group of related acids. [c] This study. [d] Ref. 20. [e] Ref. 4. [f] Ref. 5. [g] Ref. 11. [h] Ref. 14. [i] Ref. 6. [j] Ref. 23 reports 87%. [k] Ref. 6 reports $\alpha = 0.66$. We find with 4.2 *M* water, $k = 2.5$, $\alpha = 0.62$; with 1.7 *M* methyl benzoate, $k = 0.72$, $\alpha = 0.85$. [l] Ref. 21. [m] Ref. 19.

One other observation is pertinent. In the reaction of molecular acids which were sufficiently weak so that competition from free hydrogen ions was negligible, the product proportions ester/ether were found to be insensitive to the addition of salts of the acid.[20] This indicated that competition between solvent molecules and the anion of the acid for free diazonium or carbonium ion intermediates occurred at no point along the reaction path leading to the ester.

Table II

Rate, Isotope Effect, and Product Composition Data in the Reaction of Benzoic Acid with Diphenyldiazomethane in Ethanol[a]

Temp., °C.	Acid, mole l.$^{-1}$	α	k, l. mole^{-1} min.$^{-1}$
C_6H_5COOH–C_2H_5OH	0.0528		0.218
13.6 ± 0.2	.1055		.225
	.1846		.245
	.369		.284
	.528		.333
	.659		.332
26.05 ± 0.1	.0316		.72
	.0316		.74
	.0632		.75
	.0632		.77
	.1422		.79
35.35 ± 0.1	.01584	0.59	...
	.01600	.64	...
	.01978	.63	1.69
	.02000	.64	1.65
	.02967	.63	1.69
	.03956	.62	1.57
C_6H_5COOD–C_2H_5OD	.01543	.63	...
35.35 ± 0.1	.01877	.68	0.43
	.01929	.64	.47
	.02893	.68	.49

[a] At 35.35°, for C_6H_5COOH mean $\alpha = 0.63 \pm 0.02$, mean $k_H = 1.64$[b]; for C_6H_5COOD mean $\alpha = 0.66 \pm 0.04$, mean $k_D = 0.46$[b]. Isotope effect on reaction rate: $k_H/k_D = 3.6 \pm 0.3$. Isotope effect on product ratio: 1.05 ± 0.07. [b] The rate constants were measured at sufficiently low acid concentrations so that extrapolation to infinite dilution was unnecessary.

Table III

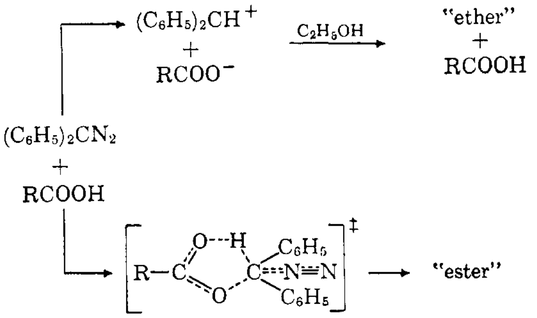
The Reaction of Diphenyldiazomethane with Benzoic Acid in Ethanol–Toluene Mixtures at 26.9 ± 0.1°

Ethanol, volume %	k_H, l. mole^{-1} min.$^{-1}$	Ethanol, volume %	k_H, l. mole^{-1} min.$^{-1}$
0.00	0.79[a]	25.8	0.46
1.37	.70[a]	44.1	.52
3.7	.52[a]	62.6	.61
7.4	.44	92.0	.73
		100	.69

[a] Benzoic acid, 0.0728 *M*. In all other runs; benzoic acid, 0.768 *M*.

On the basis of these results Roberts, *et al.*, considered a number of reaction paths of which mechanism I was thought the most probable.[19-23] This is illustrated for benzoic acid. The ester is formed *via* a three-center transition state in a single step reaction between the acid and DDM, while the ether arises from attack of a solvent molecule on a diazonium or carbonium ion intermediate.[20,21] The salient feature of this mechanism is the assumption of two parallel rate-determining steps. Several subsequent workers have followed this formulation and have partitioned their rate constants according to the ester to ether ratio in the products.[4,5]

Mechanism I



An alternative possibility, pointed out by Roberts, is that the ester is formed *via* an ion-pair intermediate.[21] Extension of this view in mechanism II suggests a

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(21) J. D. Roberts, W. Watanabe, and R. E. McMahon, *ibid.*, **73**, 2521 (1951).

(22) J. D. Roberts, C. M. Regan, and I. Allen, *ibid.*, **74**, 3679 (1952).

(23) J. D. Roberts and C. M. Regan, *ibid.*, **74**, 3695 (1952).

TABLE IV

RATE AND ISOTOPE EFFECTS IN THE REACTION OF BENZOIC ACID WITH DIPHENYLDIAZOMETHANE IN TOLUENE

Acid, mole l.$^{-1}$	Temp., °C.	k,[a] l. mole^{-1} min.$^{-1}$	k_H/k_D[b]
C_6H_5COOH			
0.0528	13.6 ± 0.2	0.218	
.1055		.225	
.1846		.245	
.369		.284	
.528		.333	
.659		.332	
C_6H_5COOD[d]			
0.0606		0.094	2.9
.0705		.097	2.9
.0849		.096	2.9
.0994		.097	2.9
.1577		.086	3.4
.2427		.087	3.7
C_6H_5COOH			
0.00379	25.9 ± 0.1	0.72[c]	
.00757		.74[c]	
.01136		.77[c]	
.01515		.78[c]	
.01515		.78[c]	
.0193	26.9 ± 0.1	.74	
.0258		.76	
.0386		.77	
.0644		.81	
.0902		.83	
.1159		.87	
.1546		.90	
.2190		.93	
.2840		.93	
C_6H_5COOD[d]			
0.0194	26.9 ± 0.1	0.385	1.8
.0267		.347	2.1
.0323		.351	2.1
.0540		.276	2.8
.0544		.315	2.5
.0583		.297	2.7
.0755		.278	2.9
.1080		.266	3.2
.1080		.249	3.4
C_6H_5COOH			
0.0180	35.5 ± 0.1	1.39	
.0239		1.48	
.0359		1.49	
.0598		1.54	
.0837		1.58	
.1196		1.64	
C_6H_5COOD[b]			
.0142		0.76	1.8
.0284		.67	2.2
.0442		.58	2.6
.0851		.57	2.8
.1700		.53	
.2270		.54	
.2840		.53	
.3550		.54	

[a] k was determined under pseudo-first-order conditions unless otherwise stated. [b] Values of k_H interpolated. [c] Determined under second-order conditions. Allowing for the temperature difference, these k's are consistently *ca.* 15% higher than those determined under pseudo-first-order conditions. The reason for this is not clear. [d] Rate constants are corrected for the presence of up to 5% C_6H_5COOH.

TABLE V

ESTIMATED PROPORTIONS OF BENZOIC ACID MONOMERS AND DIMERS AT VARIOUS ACID CONCENTRATIONS IN TOLUENE FOR TWO ASSUMED VALUES OF THE ASSOCIATION CONSTANT

Benzoic acid, mole l.$^{-1}$	Proportion of dimers	
	$K^a = 2 \times 10^{-4}$	$K^b = 5 \times 10^{-4}$
0.001	0.60	0.44
.015	.92	.88
.020	.93	.895
.25	.98	.97
.35	.983	.973

[a] The association constant for benzoic acid in benzene at 30°, ref. 44. [b] Arbitrarily chosen to indicate the sensitivity of the dimer concentration to the value of the association constant.

TABLE VI

THE REACTION OF BENZOIC-*h* ACID AND BENZOIC-*d* ACID WITH DIPHENYLDIAZOMETHANE IN TOLUENE IN THE PRESENCE OF ETHANOL AND METHYL BENZOATE

Solvent, mole l.$^{-1}$	k_H, l. mole^{-1} min.$^{-1}$	k_D,[a] l. mole^{-1} min.$^{-1}$	k_H/k_D
Methyl benzoate[b]			
0	0.82	0.234	3.5
0.281	.84	.232	3.6
.492	.84	.243	3.5
.773	.86	.243	3.5
1.055	.87	.238	3.7
Ethanol[c]			
0	0.83	0.275	3.0
0.312	.77	.230	3.4
.624	.65	.192	3.4
.936	.57	.170	3.4
1.56	.51	.147	3.5

[a] For added ethanol, k_D was interpolated from a graph of k_D *vs.* concentration of C_2H_5OD. For added methyl benzoate, k_D is corrected for the presence of 4.8% undeuterated acid. [b] Benzoic-*h* acid, 0.1234 *M;* benzoic-*d* acid, 0.1197 *M;* temp. = 26.3 ± 0.1°. [c] Benzoic-*h* acid, 0.1260 *M;* benzoic-*d* acid, 0.1382 *M;* temp. = 26.9 ± 0.1°.

TABLE VII

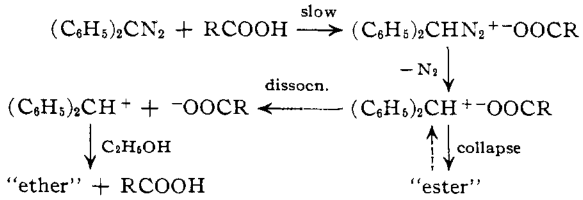
ACTIVATION PARAMETERS FOR THE REACTION OF DIPHENYLDIAZOMETHANE AND BENZOIC ACID

Solvent	Acid, mole l.$^{-1}$	ΔH^*, kcal. mole^{-1}	$-\Delta S^*$, cal. deg.$^{-1}$ mole^{-1}
	C_6H_5COOH		
Ethanol	0[a]	15.8	7
Toluene	0.015	13.1[b]	14
	.04	13.3	12
	.12	14.0	10
	.26	13.1	13
	C_6H_5COOD		
Toluene	0.02	12.9[b]	18
	.06	13.8	15
	.14	14.1	14
	.26	14.1	14

[a] Extrapolated to infinite dilution. [b] Measurements at two temperatures only; otherwise, rate constants were measured or interpolated at three temperatures.

mechanism involving a single rate-determining step leading to the intermediate formation of benzhydryl carbonium ion pairs which determine the product ratio of ester to ether by their relative tendencies to collapse or dissociate. The dotted arrow represents the possibility that the ester product is hydrolyzed at a rate comparable to that of the over-all reaction.[19,24,25]

Mechanism II



Two lines of evidence suggest that the existence of parallel rate-determining steps of mechanism I is im-

TABLE VIII
RATE AND PRODUCT COMPOSITION DATA FOR THE REACTION OF SEVERAL ACIDS WITH DIPHENYLDIAZOMETHANE IN ETHANOL AT 25.85°[a]

Acid, mole l.$^{-1}$ × 10^3		DDM, mole l.$^{-1}$ × 10^3	α	k, l. mole^{-1} min.$^{-1}$
Acetic	37.22	3.32		0.406
	22.33	3.62		0.437
	31.05	8.97	0.66[b]	. . .
	52.18	8.97	.67[b]	. . .
	5.583	3.32	.64	0.423
	33.50	23.9	.68	0.409
Formic	23.98	3.62		1.66
	23.98	2.21		1.57
	33.56	5.86	0.80[b]	. . .
	46.57	9.78	.77[b]	. . .
	3.597	3.62	.83	1.83[c]
	21.58	15.3	.83	1.68
	21.28	23.9	.76	1.63
	23.65	19.9	.79	1.62
2,6-Dinitrophenol	3.580	1.97	.68[d]	7.62[d]
2,4-Dinitronaphthol	5.105	1.97	.35	7.53
	5.105	2.27	.39	7.71
	5.105	2.31	.33	7.49
	3.695	2.91	.14	7.89
	3.230	3.66	.16	8.78
	3.088	3.50	.17	8.96
	1.938	3.50	.08	9.29
	1.853	3.50	.06	9.49
	1.235	3.50	.05	9.81
p-Nitrobenzoic	11.10	14.4	.65[e]	. . .
	25.6	≃2.0	. . .	3.60[f]
p-Methoxybenzoic	12.77	15.5	0.66[g]	. . .
	9.80	≃2.0	. . .	0.47[h]
Crotonic acid	54.7	≃2.0	. . .	0.46[i]
Phenylpropiolic acid	13.7	≃2.0	. . .	14.8

[a] Most kinetic runs were carried out under pseudo-first-order conditions to obtain k's. The product ratio α was obtained from eq. 5 unless otherwise noted. [b] α by acid titration. [c] Because of the near equivalence in the concentration of the reactants, k cannot be determined accurately. [d] Typical of seven runs: mean α = 0.68, k = 7.81. [e] Typical of three runs: mean k = 0.66. [f] Typical of three runs: mean k = 3.60. [g] Typical of three runs: mean k = 0.46. [h] Typical of three runs: mean k = 0.47. [i] Typical of three runs: mean k = 14.6.

plausible. Both concern influences on α, the fraction of ester in the product,[26] through the effect of changes in the structure and reactivity of the acid and in the deuteration of acid and solvent.

In Table I are listed values of α for a number of acids. These range from 0.6–0.7 and as some of the acids, *e.g.*, 2,6-dichlorobenzoic and 1,4-cyclohexanecarboxylic, are representative of a group of related compounds, these limits are characteristic of perhaps fifty acids.[4-6,11,14] This invariance of the α-values for acids of quite widely varying structure and reactivity provides the best evidence for a mechanistic distinction between schemes I and II. For, if indeed the reaction proceeds by parallel rate-determining steps, it would be expected that the difference between the two transition states would be manifested in different energetic responses to structural and electronic influences in the reactants. The activation energies would be of the order of 15 kcal. mole^{-1} (Table VII), and this is sufficient to require some degree of selectivity of the DDM.[11,14] In fact, the marked lack of selectivity suggests that partitioning occurs by processes of low activation energy, and, hence, subsequent to the rate-determining step. This is borne out by the fact that in most cases α varies but little with change of temperature, <2%, even in a 50° temperature range[6,14]; in one other study an average increase in α of 7 ± 4% for seven 2-furoic acids was found for a 10° drop in temperature.[11]

The same conclusion is reached from consideration of the primary hydrogen isotope effect on the product ratio α. According to scheme I, each of the two rate-determining steps involves proton transfers between the same reactants and the hydrogen isotope effect should provide a sensitive means of distinguishing them. In Table II, the α-values found for the reaction of protio- and deuteriobenzoic acids with DDM are compared. The reaction of the deuterio acid was carried out in deuterated solvent and is the slower by a factor of 3.6, which is in agreement with Roberts' previous determination.[22] However, the deuterio acid gives 66% ester in the products which is within experimental error of the value for the protio acid. This means that the isotope effect on each of the partitioning steps must be very nearly the same. While this does not exclude mechanism I, it does require an improbable canceling of the vibration frequencies sensitive to deuterium substitution between the two transition states. A more natural conclusion is that the reaction proceeds with a slow step common to both reaction paths which is followed by a partitioning process that does not involve proton transfers.

It should be mentioned that there are perhaps three acids whose α-values in ethanol are "abnormal" (in other solvents, α varies more widely with acid structure, as well as from solvent to solvent[6]). Molecular hydrogen chloride is not considered one of these: it does produce both benzhydryl chloride and benzhydryl ethyl ether but the chloride solvolyzes at a rate comparable to the DDM reaction.[19] We have found low α-values for the reaction of 2,4-dinitronaphthol with DDM in ethanol (Table I). Over the initial concentration range (0.005–0.001 M) α falls from 0.4 to 0.05. Here the explanation may be that there is sufficient dissociation of the acid for appreciable reaction through solvated hydrogen ions which give exclusively benzhydryl ethyl ether. No measurement of the pK in ethanol appears to have been made, but these results are consistent with Roberts' observation of a contribution from hydronium ion catalysis as in the reaction of 2,4-dinitrophenol with DDM.[21] An unresolved difficulty in this argument is that 2,4- and 2,6-dinitrophenols, which are probably about as strong acids as 2,4-dinitronaphthol,[27] give normal α-values.

Roberts, *et al.*, showed that molecular picric acid does not yield any benzhydryl picryl ether (α = 0).

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[24] For anhydrous or slightly aqueous acetonitrile and perchloric acid, Bethell and Callister modified the partitioning process at the point of departure for ether formation[25]

$$\begin{tikzcd}
(C_6H_5)_2CH^+ + (C_6H_5)_2CN_2 \arrow[r] \arrow[d, "H_2O"] & (C_6H_5)_2CH(C_6H_5)_2C^+ + N_2 \arrow[d] \\
(C_6H_5)_2CHOH & (C_6H_5)_2C{=}C(C_6H_5)_2
\end{tikzcd}$$

[25] D. Bethell and J. D. Callister, *J. Chem. Soc.*, 3801, 3808 (1963).

[26] α is the fraction of combined acid in the product. We shall usually refer to this as the "ester" fraction although phenolic acids lead to phenolic ethers. For a new method of determining α, see Experimental.

[27] In water pK values at 25° are phenol (9.99), α-naphthol (9.34), 2,4-dinitrophenol (4.11), 2,6-dinitrophenol (3.7), picric acid (0.22): G. Kortüm, W. Vogel, and K. Andrussow, "Dissociation Constants for Organic Acids in Aqueous Solution," Butterworths, London, 1961. For some data in ethanol, see E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964).

As this particular picryl ether has not been reported, the question of its stability in ethanol could be raised. However, related compounds such as benzhydryl 2,4-dinitrophenyl ether or benzyl or isopropyl picryl ethers are stable under conditions probably more strenuous than those encountered in the DDM reaction.[28a] One important property of picrate ion is its low nucleophilic reactivity, lower even than chloride or fluoride, toward a saturated carbon in a hydroxylic solvent.[29] For example, picryl ethers can be made from certain alkyl iodides and silver picrate, but the use of alcohol in the solvent leads mainly to free acid not ether.[28] Within the framework of mechanism II we are compelled to conclude that in the ion pair the solvated picrate ion is sufficiently indifferent to the benzhydryl carbonium species to survive many encounters with it. This rather special explanation must be considered as tentative.

Formic acid with $\alpha \simeq 0.8$ provides an example of another kind (Table I). We cannot rationalize its high yield of ester, but in face of the large number of acids for which a near constant value of α appears normal, it seems unwarranted to weight this result unduly. The true explanation for all of the "exceptional" cases may lie in the detailed mechanism of the partitioning process which the present results do not fully elucidate.

If the rate-determining step of mechanism II is accepted, we can turn to the product-determining steps. The possibilities are that (a) dissociation may occur at the stage of either the diazonium ion or the carbonium ion pairs; and (b) that dissociation of the ion pair may be assisted by attack, either from the solvent or from added ions. These questions may be framed in a broader context since diazonium ions are known also to be intermediates in the deamination of aliphatic amines and decomposition of N-nitrosoamides. Subsequent to the formation of the diazonium ion it seems probable that all of these reactions follow one or more common paths.[30]

Consider first the loss of nitrogen from the diazonium ion. It has been suggested that bimolecular displacement of nitrogen by a solvent molecule may compete with unimolecular dissociation to the carbonium ion in the deamination of a number of primary and secondary amines that proceed with dominant inversion of configuration in aqueous solvents.[31a] This has been confirmed for the reaction of ethyl diazoacetate with strong acids, in which the dissociation of the diazonium ion is rate determining: the rate increases proportionately to the concentration of added nucleophiles.[31b]

But the DDM reaction is different. Added nucleophiles do not affect the rate law of the slow proton transfer although ordinary salt effects are in evidence.[20] Though there are small changes in the ester fraction on the addition of strong nucleophiles, *e.g.*, thiocyanate and iodide, product diversion is less here than in the solvolysis of benzhydryl chloride under similar conditions.[20] Therefore, it seems highly improbable that nucleophiles are either facilitating the dissociation of the diazonium ion pair or assisting in the ejection of nitrogen. The contrast with ethyl diazoacetate is rationalized on the basis that DDM produces the relatively stable benzhydryl carbonium ion. And just as the corresponding benzhydryl halides solvolyze predominantly by S_N1 processes,[32] so too it is probable that the benzhydryl diazonium ion sheds nitrogen by unimolecular dissociation. The lower activation energy of the nitrogen loss, less by *ca.* 10 kcal. mole^{-1}, supports this view.[18]

The formation of the diazonium ion and carbonium ion within ion pairs is corroborated by studies of deamination and N-nitrosoamide decomposition.[33-36] The closest parallel to this portion of mechanism II is found in a detailed study of the thermal decomposition of optically active N-(1-phenylethyl)-N-nitroso-2-naphthamide labeled with ^{18}O in the carbonyl position.[35] White and Aufdermarsh showed that the products of this reaction in a variety of solvents, including methanol, comprised 1-phenylethyl naphthoate together with olefin and solvolysis products. The naphthoate ester was formed with predominant retention of configuration and only partial ^{18}O equilibration—the extent of equilibration being independent of the extent of racemization of the ester. A further observation in the reactions of a number of N-nitrosoamides was that the extent of racemization and degree of ^{18}O equilibration in the ester product is remarkably insensitive to changes of temperature and electronic influences in the alkyl group.[35,36] The DDM reaction displays the same sort of insensitivity and this suggests a marked lack of discrimination in the partitioning of the ion-pair intermediates. Taken together, these results require the intermediacy of a diazonium ion pair and that nitrogen be lost without disruption of the ion pair as in mechanism II.

A first explanation of these results for a *single* solvent, ethanol, is that *the product proportions are controlled by the rate of diffusion of paired ions out of their solvent cage at the stage of the carbonium ion pair.*[37] The fact that α is essentially independent of structural factors and external nucleophilic ions is consistent with such a process. White's finding that the degree of rotation of the carbonium ion prior to ion-pair collapse in the N-nitrosoamide reaction is determined by the bulk of the ion—that is, larger ions show a smaller degree of racemization[34]—is also consistent with diffusion control of the products.

When one considers α for the DDM reaction in other solvents, the details of the partitioning can be refined. Consideration of three interrelated factors makes it possible to pull together disparate observations on the product-determining steps. Bowden, *et al.*, report that the ester fraction decreases as the *nucleo-*

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(28) (a) G. E. Philbrook and D. J. Massey, *J. Am. Chem. Soc.*, **73**, 3454 (1951); (b) G. Kumpf, *Ann.*, **224**, 96 (1884); C. L. Jackson and F. H. Gazzolo, *Am. Chem. J.*, **23**, 376 (1900).

(29) A. J. Parker, *J. Chem. Soc.*, 1328 (1961).

(30) J. H. Ridd, *Quart. Rev.* (London), **15**, 418 (1961).

(31) (a) P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold, and P. A. D. S. Rao, *Nature*, **166**, 179 (1950); A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957); (b) W. J. Alberry and R. P. Bell, *Trans. Faraday Soc.*, **57**, 1942 (1961).

(32) O. T. Benfey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2488 (1952). The solvent here was 80% aqueous acetone.

(33) (a) R. Huisgen and C. Ruchardt, *Ann.*, **601**, 1, 21 (1956); (b) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 286 (1935); (c) D. Y. Curtin and S. M. Gerber, *J. Am. Chem. Soc.*, **74**, 4052 (1952).

(34) E. H. White and J. E. Stuber, *ibid.*, **85**, 2169 (1963).

(35) E. H. White and C. A. Aufdermarsh, *ibid.*, **83**, 1179 (1961).

(36) E. H. White, *ibid.*, **77**, 6014 (1955); E. H. White and D. W. Grisley, *ibid.*, **83**, 1191 (1961). The widest temperature range was covered with an N-nitroamide, the rearrangement of which proceeds by a similar mechanism to the N-nitrosoamides.

(37) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 106 ff., and references cited therein.

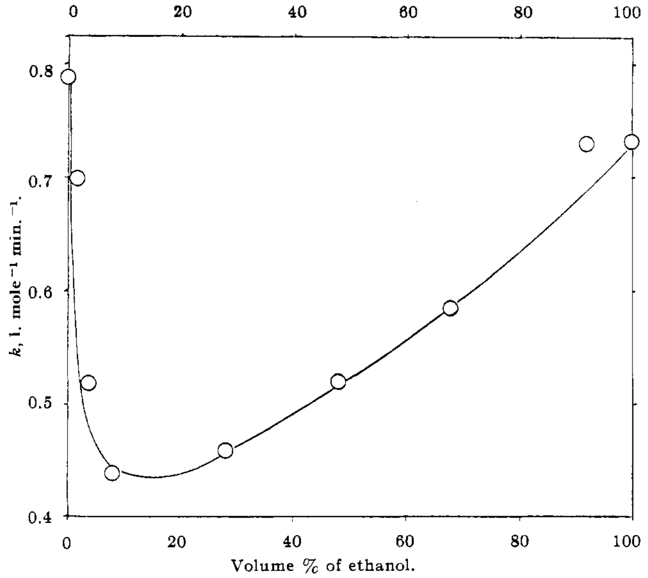
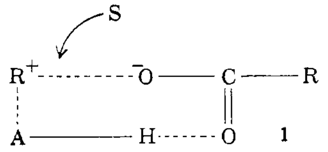


Fig. 1.—The reaction of benzoic acid with diphenyldiazomethane in ethanol–toluene mixtures.

philic character of the solvent increases: thus, the average α-values for several substituted benzoic acids in two solvent series are in *t*-butyl alcohol (0.45–0.54), ethanol (0.60), and 2-methoxyethanol (0.70), and in *p*-methoxybenzyl alcohol (0.46–0.58), benzyl alcohol (0.62–0.77), and *p*-nitrobenzyl alcohol (0.72–0.90).[6] Both our work and previous work show that the *polarity* of the solvent is important: dilution of ethanol with water leads to less ester in the reaction of DDM with phenylacetic (Table I) or with benzoic acids[20]; as compared with tetrahydrofuran[33a] or acetic acid,[35] the more polar methanol leads to less ester in the nitrosoamide decompositions. Thirdly, exchange with external acid has been observed in the nitrosoamide reaction where the *stronger the acid* the more likely it is to be found in the ester product.[36]

In summary we believe that the partitioning process is best described in mechanism II. Collapse to ester or separation to free acid and ether occurs at the carbonium ion-pair stage, that is from the species **1** where HA is either acid or solvent and where S is the



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solvent. Any pictorial representation of the influences on ion-pair collapse *vs.* separation by *diffusion* must be inadequate, but **1**, which evolved from more specific models,[6,35] is intended to show that three environmental factors—nucleophilicity, polarity, and acidity—influence the product-determining steps of the DDM reaction.

Now it has been suggested that because nitrogen loss is often exothermic, the carbonium ion pair may be "hot."[18] Whether or not this condition is a factor in the product partitioning can be determined by comparing identical ion pairs generated in the same medium by nitrogen loss or solvolysis. Heretofore, this comparison has been difficult for several reasons: the counter-ions of solvolysis have differed from those in deamination; different timings may have been involved in rearrangement and elimination paths, where these have occurred; and for relatively unstable carbonium ions, dissociation may have occurred at the diazonium ion stage.[30] Because it is free from these complications, the decomposition of DDM would provide a particularly simple example for comparison with a solvolysis reaction.[38] Identical product partitioning in each case, that is, between ion-pair dissociation and collapse (return), would strongly indicate that the detailed interpretation of mechanism at the carbonium ion-pair stage should also be identical.

Medium Effects on the DDM Reaction in Ethanol.—In ethanol the reaction is accurately first order in DDM, and small changes in acid concentration indicate that it is first order in benzoic acid also. However, the second-order rate constant increases by 50% as the concentration of benzoic acid increases from 0.05–0.7 *M* (Table II). This concentration effect is important in relation to structure–reactivity studies, since it approaches the magnitude of a normal substituent effect. It is therefore necessary either to extrapolate rate data to infinite dilution or to make measurements at a sufficiently low acid concentration so that the rate constant deviates only slightly from the extrapolated value.[7]

The cause of the increased reactivity may be that the medium is more polar. Alternatively, and more specifically, it may be a consequence of the formation of *benzoic acid dimers*. From results in toluene and ethanol–toluene mixtures (*vide infra*), it is clear that the reactivity of acid dimers toward DDM is *greater than that of monomers*, which presumably form the predominant acidic species in a hydrogen-bonding solvent as polar as ethanol.

The rate profile of the benzoic acid–DDM reaction in ethanol–toluene mixtures shown in Fig. 1 (Table III) gives an intimation of the importance of dimers and of their enhanced reactivity. The decrease in the reaction rate on the addition of small quantities of toluene to ethanol may be attributed to a medium effect on the monomeric acid. This is the expected result of diminished solvent polarity since proton transfer between uncharged reactants, as in the DDM reaction, involves charge separation in the transition state.[39] However, as the concentration of toluene is increased, the rate constant passes through a minimum and increases again to the value in pure toluene. We believe that the rate increase is consistent with a rise in concentration of dimers whose greater reactivity more than compensates the adverse medium effect.[40] The decrease in the rate constant of the reaction of phenylacetic acid with DDM in ethanol on the addition of methyl benzoate (1.7 *M*, Table I, footnote *k*) and the increase in the rate constant of the benzoic acid–DDM reaction in ethanol with substantial amounts of chloroform (29%) or benzene

(38) Recent evidence for the existence of ion pairs containing the benzhydryl carbonium ion and chloride, acetate, *p*-nitrobenzoate, or thiocyanate ions has been given: S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960); A. F. Diaz and S. Winstein, *ibid.*, **86**, 4484 (1964); H. L. Goering and J. F. Levy, *ibid.*, **86**, 121 (1964); H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, **85**, 3059 (1963); A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *ibid.*, **83**, 2729 (1961).

(39) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 453 ff.

(40) Similar rate profiles have been observed for other systems in solvent mixtures and have likewise been interpreted in terms of a balance between a medium effect and association; A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 33; J. W. Hackett and H. C. Thomas, *J. Am. Chem. Soc.*, **72**, 4962 (1950).

(29%)[20] can be explained in the same way. The fact that water (Table I, footnote *k*), nitrobenzene, and indifferent salts all increase the DDM rate[20] is consistent with an increased polarity or dielectric constant of the medium.[20,39]

Detailed consideration of the source of the enhanced acidity brought about by dimerization will be deferred until its scope is further defined. Together with the parallel effect of solvent polarity, it will form the basis of discussion of reactivity in toluene. While both effects are inadequate to explain all the data, there is evidence for the importance of each.

Medium Effects on the DDM Reaction in Toluene.— In toluene, the reaction with benzoic acid should yield, almost quantitatively, benzhydryl benzoate[41]; another possible product is tetraphenylethylene.[25] The kinetic order with respect to DDM remains accurately unity, but the formal order with respect to acid is concentration dependent as it is in several other aprotic solvents.[41] The effect is larger than that observed in ethanol and amounts to a 30% increase in the apparent second-order rate constant over the range 0.02–0.2 *M* in benzoic acid (Table IV). The situation is complicated by the fact that for the reaction of deuteriobenzoic acid with DDM in toluene the rate constant *decreases* with acid concentration (Table IV). As may be seen from Fig. 2, this leads to an unusual dependence of the kinetic isotope effect on acid concentration: over the range 0.015–0.2 *M*, k_H/k_D increases from 1.8–3.7!

To what extent can we ascribe these trends in the rate constants to changes in the carboxylic acid monomer–dimer concentrations?[42–45] Drawing on the extensive association data of benzoic acid in benzene, it can be shown (Table V) that the change in the proportion of dimers over the concentration range of acid studied is probably too small in toluene to account for more than a fraction of the change in the rate constants. Clearly, there is a substantial medium effect in toluene independent of the question of acid association and the reactive acid species.

The conclusion that these effects do *not* derive from changes in acid association is supported by measurements of hydrogen isotope effects on carboxylic acid association constants. Again, no data are available for toluene, but a number of reports of K_H/K_D for the association of acids in the gas phase give values within experimental error of unity (a single measurement in benzene gives $K_H/K_D = 1.25$ for acetic acid).[43] Thus, at the concentrations of benzoic acid used in toluene, the association of the protio and deuterio acids can hardly be significantly different. Furthermore, in Table VI is shown the effects of adding ethanol and deuterioethanol to toluene. Increase in ethanol concentration is known to decrease substantially the dimer–monomer ratio and a decrease in rate is observed. However, the isotope effect on the reaction rate is sensibly unchanged. Similar behavior was found for the addition of methyl benzoate, though in this case changes in k_H and k_D were very small (Table VI). While at present we have no positive explanation for these medium effects, it does seem clear that they are not the result of acid association equilibria.

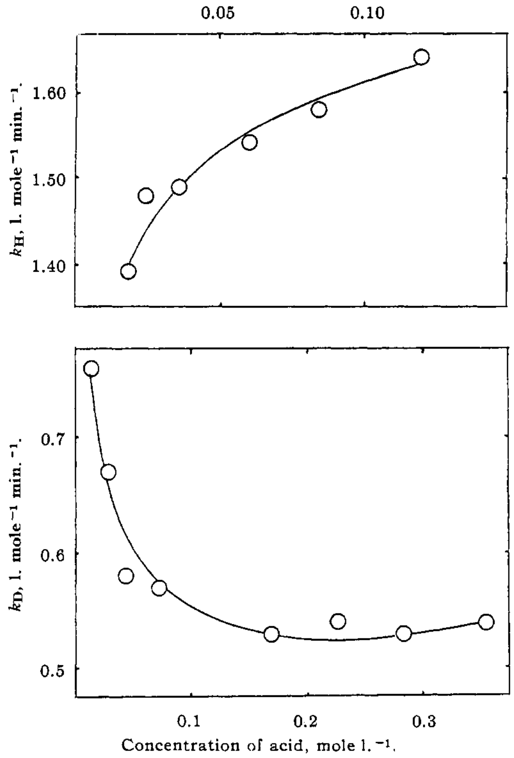

Fig. 2.—The dependence of the reactions of benzoic-*h* acid and benzoic-*d* acid with diphenyldiazomethane on the concentration of acid at 35.5 ± 0.1°: upper curve for benzoic-*h* acid; lower curve for benzoic-*d* acid.

Returning now to behavior that does appear to depend on acid association, we know that in toluene the predominant acidic species must be the dimer. Further, the rate minimum in ethanol–toluene mixtures was rationalized on the basis that the benzoic acid dimer is more reactive than the monomer. Support for this hypothesis also comes from a comparison of Hammett plots (Fig. 3) for a series of substituted benzoic acids in ethanol and toluene. The first point to be noted is that not only are the rates of reaction of benzoic acid with DDM nearly the same in the two solvents (see also Tables II, IV), but for more reactive acids, such as *p*-nitrobenzoic, the rate is greater in the less polar solvent. This is the opposite to what would be expected on the basis of changes in polarity and solvation power of the medium alone.

A second feature of Fig. 3 is the marked difference in the Hammett reaction constants: $\rho = 2.51$ in toluene and $\rho = 0.93$ in ethanol.[46] (In 40% ethanol and 0.1 *N* sodium chloride, $\rho = 0.7$ and the rate constant has increased by a factor of *ca.* 3 over that in pure ethanol.[17b]) The discrepancy between the ρ-values in ethanol and toluene is important because, if there is no change in mechanism, variations in ρ should arise primarily through solvent interactions at the reaction site. This, however, would require at least a qualitative relation between the magnitude of ρ and the

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(41) J. D. Roberts and C. M. Regan, *Anal. Chem.*, **24**, 360 (1952). In benzene the DDM rate constant changes by *ca.* 20% and *ca.* 70% for twofold changes in concentration of acetic acid and chloroacetic acid, respectively. "Nonintegral" order in acid is also reported for the solvents chloroform, ethylene dichloride, acetonitrile, and acetone.

(42) G. Allen and E. F. Caldin, *Quart. Rev.* (London), **7**, 255 (1953).

(43) G. C. Pimentel and A. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp. 211, 369.

(44) F. T. Wall and W. F. Banes, *J. Am. Chem. Soc.*, **67**, 898 (1945).

(45) M. M. Davies and H. B. Hetzer, *J. Natl. Bur. Std.*, **60**, 569 (1958).

(46) A similar discrepancy is observed for the rates of aliphatic carboxylic acids with DDM in ethanol and toluene. Plots of rate constants *vs.* σ^* give $\rho^* = 2.80$ in toluene and $\rho^* = 1.18$ in ethanol.[18] Furthermore, the *equilibrium* protonation of diphenylguanidine by *m*-substituted benzoic acids in benzene leads to $\rho = 2.17$.[45]

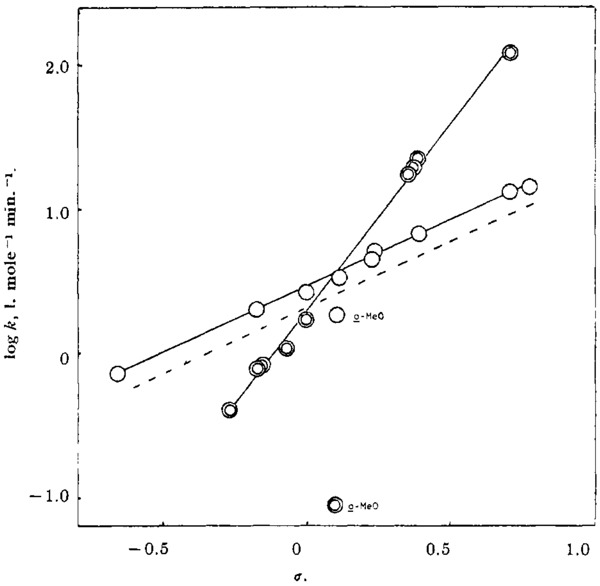
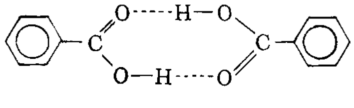


Fig. 3.—Hammett plots for the reaction of diphenyldiazomethane with substituted benzoic acids: circles, at 30° in ethanol[20]; bullseyes, at 25° in toluene.[3] (Rate data in ethanol have been extrapolated to 25° on the assumption that the activation energies of all of the acids are equal to that of benzoic. The extrapolation is represented by the dotted line. The *o*-CH_3O points are from ref. 6 for ethanol and from ref. 3, 48 for toluene. The σ used for *o*-CH_3O– was 0.11 and was based on the p*K* of the acid in water.[45])

reactivity of acids. But between ethanol and toluene there is no significant change in reactivity—the cross-over point in Fig. 3 illustrates this point concretely. Therefore the enhanced ρ represents an extra electronic influence of the substituents on the reaction over and above that in ethanol. This can be rationalized simply on the assumption that the reactive acidic species in ethanol is the monomer and in toluene it is the dimer. The dimer may be represented as **2** and its transition state in the DDM reaction as **3.**



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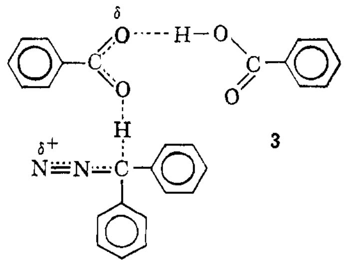

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Initially, the notion that the acid dimers should be more reactive than the monomers may appear unlikely. Association of the acid will increase the stability of the ground state by reducing the accessibility of the acidic hydrogen through hydrogen bonding. However, it seems probable that the effect is offset in the transition state by the opportunity for hydrogen-bonded interaction with the negative charge developing on the carboxyl group from which a proton is being transferred as in **3**. Because the hydrogen bond in the transition state is donated to a partially charged oxygen, while that in the ground state is donated to a neutral oxygen dimerization should lead to a greater energy reduction in the transition state and, hence, an over-all increase in reactivity. Similarly, the influence of substituents on the reactivity of the dimer is twofold. first, an effect on the acidity of the proton undergoing transfer in the reaction and, second, an effect on the hydrogen bond facilitating the development of charge on the incipient carboxylate anion. The two effects, being favored by electron-withdrawing substituents, are complementary and require the observed increase in ρ as the reacting species changes from monomer to dimer.

One acid that is known not to be appreciably dimerized at these concentrations in benzene, presumably because of intramolecular hydrogen bonding, is 2-methoxybenzoic acid.[45,47] Significantly, this acid shows a greater decrease in reactivity on passing from ethanol to toluene than any other acid whose rate constants have been measured in both solvents so far.[48] Judging from its p*K* relative to that of benzoic acid,[45] 2-hydroxybenzioc acid also has a low reactivity toward DDM in toluene.[49] Though the DDM reaction could be facilitated by intramolecular hydrogen bonding, ionization of the proton in ethanol should be favored to an even greater degree; in the interaction with the 2-OH, the carboxylate anion bears a full negative charge while that on the transition state is partial. On the other hand, there is an anomalously high rate for 1-α-hydroxybenzyl-1′-ferrocenoic acid[12]: here the p*K* determined in 50% aqueous ethanol is not likely to be much affected by intramolecular hydrogen bonding since the acidity of the benzylic OH will be too low to compete with hydrogen bonds from the solvent. In toluene no such competition exists and intramolecular hydrogen bonding in the DDM transition state is entirely plausible.[49]

Davies and Hetzer have found that the apparent acidity of benzoic acid in benzene increases as the concentration of acid increases (*ca.* 10^{-3}–10^{-4} *M*).[45] This is consistent with the greater reactivity of the benzoich acid dimers in the more concentrated solutions. At sufficiently low acid, the proportion of monomer should become dominant. We hoped to observe a similar trend in the rate constant for reaction with DDM. Unfortunately, below an acid concentration of 10^{-3} *M*, the reaction rate became too slow and the change in optical density of DDM too low for measurements to be made. Even at this concentration, the proportion of dimers may be estimated as *ca.* 60% (Table V). This is not sufficiently low to introduce large changes in the rate constant with moderate changes in acid concentration, even if the monomer and dimer differ greatly in reactivity. A fall in rate constant was indeed observed, but the influence of acid association could not be separated from that of a superimposed medium effect that becomes dominant at higher acid concentrations (*vide supra*).

The effect of added methyl benzoate on the reaction rate in toluene proved inconclusive. Despite a report that the concentration of dimeric benzoic acid in ethyl benzoate is relatively low,[47] we found that methyl benzoate had little, if any, effect on the rate constants

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(47) M. Davies and D. M. L. Griffiths, *J. Chem. Soc.*, 132 (1955).

(48) J. F. Norris and W. H. Strain, *J. Am. Chem. Soc.*, **57**, 187 (1935).

(49) The interpretation here on the salicylic acid differs from that of ref. 12. In the hydroxyferrocenoic acid the rate increase was attributed to interannular bonding which freezes out the rotation of the carboxyl group.[12]

for either benzoic acid-*h* or acid-*d* (Table VI). If indeed there was an effect on the monomer–dimer ratio, it did not appear to be reflected in the rate data.

No firm evidence can be adduced for the dimer hypothesis from the activation parameters in the two solvents (Table VII). Nevertheless, it is noticeable that there is a significant difference in the balance of enthalpies and entropies of activation. The diminished entropy of activation in toluene would seem consistent with the view of a second acid molecule firmly bonded in the transition state for reaction of the dimer.

In conclusion, it may be claimed that the detailed mechanism of the DDM reaction 1 in hydroxylic solvents is now fairly well understood. For the reaction in toluene the situation is less satisfactory. The evidence from the products, kinetics, and hydrogen isotope effect suggest that there is no change in rate-determining step from the proton transfer established for the solvent ethanol. Furthermore, there is strong indication that the reactive acidic species in toluene is the dimer. On the other hand, the concentration dependence of the rate constant on acid and the associated trend in the hydrogen isotope effect are not understood or accounted for.

Experimental

Diphenyldiazomethane was prepared by a standard method. Its purification and the determination of the extinction coefficient of its absorption maximum ($\epsilon_{\max} = 102$ at 525 mμ) have been described previously.[7] So too have the details of kinetic measurements of its reaction with carboxylic acid, both in ethanol and toluene, been given. All kinetic runs were followed spectrophotometrically using a Beckman Model DK-2 automatic recording spectrophotometer.[7]

Toluene was purified by distillation from sodium and stored in a tightly stoppered bottle. The benzoic acid was of primary standard quality. Commercially available absolute ethanol was used without further purification. Ethanol-*d* (98% deuterium) was obtained from Volk Radiochemical Co.

Benzoic-*d* acid was prepared from benzoyl chloride (purified by distillation) by heating under reflux for 2 hr. with 99.8% D_2O in the absence of moisture. The acid was sublimed and stored in a desiccator. Samples were used within a few days of preparation. Before standard solutions were prepared, the deuterium content of the acid was determined from its infrared spectrum in carbon tetrachloride. The OH peak at 1425 cm.$^{-1}$ was used for analysis and its extinction coefficient determined from spectra of the undeuterated acid. The measurements were made with a Perkin-Elmer Model 21 recording spectrophotometer. The proportion of benzoic-*h* in the deuterio acid varied from 3–9%, and all rate constants had to be corrected for its presence. After correction, different samples of acids with different deuterium contents gave reproducible rate constants.

Determination of α, the Product Ratio of Combined Acid to Unreacted Acid.—In the reaction of DDM with acids, acid is consumed only in the reaction path leading to an ester, and the product ratio of ester to ether may be determined by direct kinetic measurement. Under second-order conditions, the kinetic form of the reaction is expressed by the equation

$$kt = \frac{1}{(a - \alpha b)} \ln \frac{b(a - \alpha x)}{a(b - x)} \qquad (3)$$

where a is the initial concentration of acid, b is the initial concentration of DDM, and x is the amount of DDM that has reacted after time t. Following a variation of the Guggenheim procedure, one obtains

$$e^{(a - b\alpha)kT} = \frac{(a - \alpha x')(b - x)}{(a - \alpha x)(b - x')} = \frac{(a - b\alpha)/(b - x') + \alpha}{(a - b\alpha)/(b - x) + \alpha}, \text{ and} \qquad (4)$$

$$\frac{1}{(b - x')} = \frac{e^{(a - b\alpha)kT}}{(b - x)} + \frac{\alpha(e^{(a - b\alpha)kT} - 1)}{(a - b\alpha)} \qquad (5)$$

where x' is the amount of DDM reacted after time t', and $t' - t = T$, a fixed interval that should be at least as great as one half-life. Plots of $1/(b - x')$ *vs.* $1/(b - x)$ yield a straight line. From its intercept i and slope m, both k and α may be determined.

$$\alpha = \frac{ai}{m - 1 + bi} \qquad k = \frac{2.303 \log m}{(a - b\alpha)T} \qquad (6)$$

Previous measurements of α have been made by reaction of a known quantity of DDM with acid and titration of the excess acid after the reaction was complete. However, the present method is readily applicable even with acids of low solubility or if only a small amount of solvent is available, as was the case for our measurements in deuterioethanol. Since the concentration of DDM is estimated spectrophotometrically, the magnitude of α is determined by the choice of its extinction coefficient. The accepted value for $\epsilon_{525\ \mathrm{m}\mu}$ is 95[19]; measurements in this laboratory indicate that this is probably low, and we have corrected all product ratios recorded here by using the value $\epsilon = 102$.[7] α-Values determined both kinetically and titrimetrically gave fair agreement. Typical data are given in Table VIII.

Acknowledgment.—We wish to thank Professor Chapman and his co-workers for an interesting discussion and for a preprint of their paper.[6] The experimental data in our paper and in theirs are complementary. Although there is essential agreement on the rate-determining step of the DDM reaction, the views on the partitioning steps differ.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINN., AND THE UNIVERSITY OF CHICAGO, CHICAGO, ILL.]

Conformations. VI. Vinyl–Allylic Proton Spin Couplings

BY EDGAR W. GARBISCH, JR.[1]

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Three- (J_3) and four-bond (J_4) vinyl–allylic proton spin couplings have been estimated for a series of olefinic substrates by considering σ- and π-bond contributions to both couplings as a function of allylic proton conformations. The qualitative agreement between observed and estimated couplings suggests that π-bond contributions to J_3 and σ-bond contributions to J_4 are important and should not be neglected in approximating allylic proton conformations.

The assumption has been made often[2] that the magnitudes of both the three- and four-bond vinyl–allylic proton couplings will follow a $\cos^2 \phi$ and $\sin^2 \phi$ relationship, respectively, where ϕ is the dihedral angle be-

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[2] (a) E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4249 (1962); (b) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016 (1963); (c) L. D. Hall, *J. Org. Chem.*, **29**, 297 (1964); (d) R. M. Carman and R. D. Ward, *Australian J. Chem.*, **15**, 807 (1962); (e) ref. 4.