Halogenated Ketenes. VIII. Dihaloketene Reactivities in an Acylation Reaction[1,2]

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A kinetic study was made of the acylation of 3-pentanol with butylethyl-, dibromo-, diethyl-, dichloro-, dimethyl-, and diphenylketenes. All reactions were first order in ketene and first order in alcohol. The reactivity of the ketenes increases in the order given. The acylation of 3-pentanol with diphenylketene occurred at a faster rate in a nonpolar solvent. These results are interpreted to suggest a one-step process involving a cyclic transition state and establishes that the dihaloketenes are less reactive than diphenylketene with about the same activity as the dialkylketenes in the acylation of 3-pentanol.

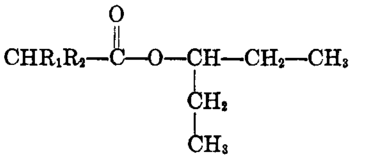
Although there is an extensive amount of literature involving the acetylation of alcohols with ketene, the acylation of alcohols with other ketenes has received much less attention. Staudinger has shown wide differences in reaction rates between different ketenes, *e.g.*, diphenylene > diphenyl > phenylmethyl > dimethyl.[3] However, this is a general reaction of ketenes and it is catalyzed by both acids and bases.

Except for Staudinger's early work on ketene reactivities, only quite recently have there been any reports on the kinetics and mechanism of this reaction. Pracejus and Leska have measured the kinetics of addition of C_1–C_5 aliphatic alcohols to phenylmethyl-, diphenyl-, and phenyl(α-naphthyl)ketenes in the presence of nitrogen heterocyclic compounds which act as catalysts.[4] The activity of the ketenes increases in the order shown.

Tille and Pracejus have investigated the kinetics and mechanism of some amine-catalyzed ketene acylations of alcohols.[5] The order of the reaction with respect to alcohol was reported to be strongly dependent on the temperature. Some work was also reported on the noncatalyzed reaction which is discussed later.

TABLE I

3-PENTYL ALKANOATES FROM KETENES AND 3-PENTANOL



$$CHR_1R_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\underset{\underset{\displaystyle CH_3}{|}}{\underset{\displaystyle CH_2}{\underset{|}{CH}}}{-}CH_2{-}CH_3$$

R_1	R_2	Bp, °C (mm)	Yield, %	Formula[a]	C, % Calcd	C, % Found	H, % Calcd	H, % Found
Cl	Cl	62 (1.8)	97	$C_7H_{12}Cl_2O_2$	42.21	42.24	6.03	6.05
Br	Br	66 (2.6)	89	$C_7H_{12}Br_2O_2$	29.16	29.25	4.17	4.39
C_2H_5	C_4H_9	83 (1.8)	97	$C_{13}H_{26}O_2$	72.89	73.19	12.15	11.92
C_2H_5	C_2H_5	60 (1.8)	83	$C_{11}H_{22}O_2$	70.96	71.15	11.83	11.83
C_6H_5	C_6H_5	170 (1.7)	93	$C_{19}H_{22}O_2$	80.85	81.09	7.80	7.50
CH_3	CH_3	161 (760)	96	$C_9H_{18}O_2$	68.35	68.30	11.39	11.58

[a] The respective registry numbers are 18598-96-4, 18598-97-5, 18598-98-6, 18598-99-7, 18599-00-3, 18599-01-4.

Some recent reports from this laboratory have described the preparation and chemistry of two dihaloketenes.[6–8] It became of interest to study the reactivity of these new dihaloketenes in relation to diphenylketene and some dialkylketenes in a nucleophilic addition reaction to determine if the halogen atoms exhibited much influence on this reaction. Therefore, a kinetic investigation of the acylation of an alcohol with several different types of ketenes including dichloro- and dibromoketenes was made and this paper describes the results of this study. All of the reactions were in the absence of added catalysts.

3-Pentanol was selected as the nucleophile because this alcohol reacts at an easily measureable rate in hexane with all the ketenes investigated at 25°. The rate of reaction was followed by observing the rate of disappearance of 3-pentanol by vapor phase chromatography. Methanol, ethanol and butanol were found to react too rapidly at this temperature to allow accurate rate determinations by this method. This nucleophilic addition reaction produces a 3-pentyl alkanoate as shown. A complete list of the esters produced is given in Table I.

A treatment of the rate data indicated that each nucleophilic addition reaction was first order in ketene and first order in 3-pentanol. These data are presented

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[1] Paper VII: W. T. Brady and E. F. Hoff, *J. Amer. Chem. Soc.*, **90**, 6256 (1968).

[2] Abstracted in part from the M.S. thesis of W.L. V., North Texas State University, 1966.

[3] H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, as seen in R. N. Lacey, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, p 1174.

[4] H. Pracejus and J. Leska, *Z. Naturforsch.*, *A*, **21**, 30 (1966).

[5] A. Tille and H. Pracejus, *Chem. Ber.*, **100**, 196 (1967).

[6] W. T. Brady, H. G. Liddell, and W. L. Vaughn, *J. Org. Chem.*, **31**, 626 (1966).

[7] W. T. Brady, *ibid.*, **31**, 2676 (1966).

[8] W. T. Brady and O. H. Waters, *ibid.*, **32**, 3703 (1967).

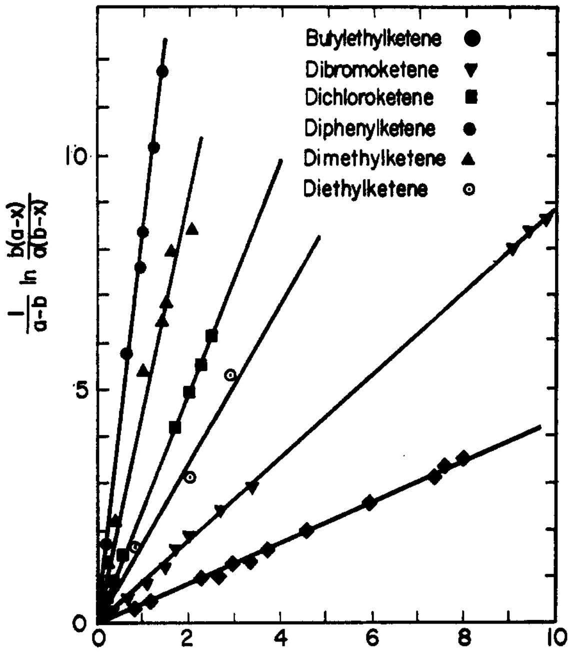
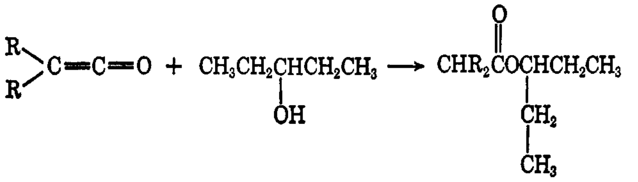


Figure 1.



$$\begin{matrix}R\\R\end{matrix}\!\!>C{=}C{=}O + CH_3CH_2\underset{OH}{C}HCH_2CH_3 \longrightarrow CHR_2\overset{O}{\overset{\|}{C}}O\underset{\underset{CH_3}{|}}{\underset{CH_2}{C}}HCH_2CH_3$$

in Figure 1. Diphenylketene reacted faster with 3-pentanol than the dialkylketenes did, as expected, and also faster than the dihaloketenes, as illustrated by the second-order rate constants given in Table II.

Table II

Second-Order Rate Constants for the Acylation of 3-Pentanol at 25° in n-Hexane

Ketene	$k \times 10^4$, l./mol sec
Diphenylketene	74 ± 2
Dimethylketene	36 ± 1.5
Dichloroketene	24 ± 1
Diethylketene	17.6 ± 0.9
Dibromoketene	9.7 ± 0.2
Butylethylketene	4.3 ± 0.1

A solvent effect study was made to determine if the solvent effected the rate of this reaction. The acylation of 3-pentanol with diphenylketene was selected for this investigation because of the ease of handling and purification of this ketene as well as the slow rate of dimerization.[9] The results are recorded in Table III.

Table III

The Effect of Solvent on the Second-Order Rate Constants for the Reaction of Diphenylketene and 3-Pentanol at 25°

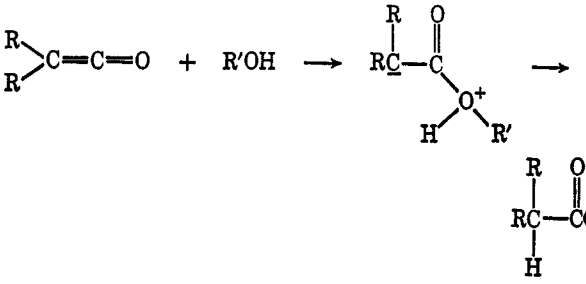
Solvent	$k \times 10^4$, l./mol sec
Hexane	74
Ether	3.3
Acetonitrile	1.7

Discussion

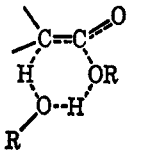
The selection of the bulky 3-pentanol as a nucleophile obviously imparts some steric problems for this reaction. However, it was desirable to slow the acylation reaction so that accurate rate data could be obtained by the method employed. It should be realized that the differences in rate between the different ketenes diminishes because of this steric effect; *e.g.*, there will be larger differences in the rates with less bulky nucleophiles. This was observed by Pracejus and Leska in studying the C_1–C_5 alcohols.[4]

The solvent effect on the second-order rate constant is real but rather small as shown in Table III. Since the rate increases with decreasing polarity of the solvent, apparently the reactants are solvated to a greater degree than the activated complex. This suggests a one-step process rather than the previously assumed two steps involving an ionic intermediate as shown in Scheme I. Furthermore, it is indicated that the transition state for this one step is less polar than the reactants, suggesting a highly ordered complex. This is consistent with the very recent findings of Satchell and Lillford who have demonstrated in an elegant fashion that the acylation of amines proceeds through a cyclic transition state.[10]

Scheme I



In the report by Pracejus and Tille, a similar solvent effect was observed.[5] Also, it was indicated that the acylation of methanol with phenylmethylketene was first order in alcohol at −80°, second order in alcohol at +1° and an order appreciably greater than two at methanol concentrations greater than 0.1 M. It was suggested that the acylation at +1° occurred through transition state A.



A

Our results involving the acylation of 3-pentanol with the ketenes investigated showed a first-order dependence on alcohol; however, in all runs only a slight excess of alcohol was used and the concentrations were always less than 0.1 M. Perhaps the order with respect to the alcohol is dependent on the steric requirements of the alcohol; *e.g.*, 3-pentanol is too big and bulky to crowd two such molecules into a cyclic transition state as shown above. Therefore, we propose that in the acylation of 3-pentanol and perhaps other bulky

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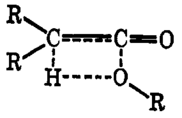
[9] There was no evidence of dimerization of any of the ketenes in the kinetic experiments.

[10] P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc.*, *B*, 54 (1968).

alcohols the reaction proceeds through a cyclic transition state B, but one involving only one molecule of 3-pentanol.



B

Our kinetic results are compatible with all of the reports in the literature which show that diarylketenes are more reactive than dialkylketenes in the acylation of alcohols. This is probably due to some degree of charge separation in the transition state and the ability of the aryl group to stabilize the activated complex by smearing out any carbanionic character at the α-carbon atom.

The smaller second-order rate constant for dibromoketene as compared to dichloroketene is exactly as expected. A consideration of both electronic and steric factors would suggest this result. The chlorine atoms are more capable of stabilizing any carbanionic character in the transition state due to the greater inductive ability and steric crowding will be more predominant with dibromoketene due to the larger bromine atoms.

The difference in rate of the three dialkylketenes would appear to be solely due to steric effects. An examination of molecular models reveals that the butyl group in butylethylketene is certainly large enough to present a steric problem for the bulky 3-pentanol molecule. Consequently, it would appear that steric considerations are the controlling factor in dialkylketene reactivities.

In conclusion, our solvent effect data suggest that the acylation of alcohols with ketenes proceeds by a one-step process which probably involves a cyclic transition state. Also, the halogen atoms in the dihaloketenes studied apparently do not markedly influence the re-reactivity of the ketene in the acylation of alcohols; *e.g.*, these ketenes exhibit about the same reactivity as dialkylketenes but both are less reactive than diphenylketene.

Experimental Section

Dichloroketene was prepared by the dehalogenation of trichloroacetyl bromide and isolated in hexane as previously described by us.[6] Dibromoketene was prepared by the dehalogenation of tribromoacetyl bromide and also isolated in hexane as one of us has previously reported.[7] Diphenylketene was prepared by the dehydrochlorination of diphenylacetyl chloride with triethylamine.[11] Diethylketene was obtained by the pyrolysis of diethylmalonic anhydride according to the procedure of Duckworth.[12] We are grateful to Eastman Chemical Products, Inc., for supplying us with butylethylketene in the form of a 20% solution in toluene. The toluene was removed under reduced pressure and the ketene distilled and dissolved in dry hexane for kinetic runs. Dimethylketene was prepared by the pyrolysis of the ketene dimer, tetramethyl-1,3-cyclobutanedione.[13]

Apparatus.—A constant-temperature water bath was employed with an immersion heating element coupled to a Fisher proportional temperature controller that afforded a temperature control of ±0.02°. The rate of disappearance of 3-pentanol was followed by vpc. An Aerograph AP-40 operating with a thermal conductivity detector was used with a 10 ft × 0.25 in. column packed with 15% Ucon and 2% Oronite on 30/60 mesh white Chromosorb. An oven temperature of 95° was employed. *n*-Octane was used as an internal standard. Least-squares rate constants were calculated on an IBM 1620 computer. Only a slight excess of 3-pentanol was employed in all runs and the concentrations ran about 0.05 *M*.

3-Pentyl Alkanoates.—A hexane solution of the ketene was treated with an excess of 3-pentanol. The hexane and excess alcohol were removed by distillation. The esters were distilled under reduced pressure through a 6 in. Vigreux column, ir absorption (smear) 1730–1770 cm^{-1}. The more detailed data are recorded in Table I.

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(12) A. C. Duckworth, *J. Org. Chem.*, **27**, 3146 (1962).

(13) W. E. Hanford and J. C. Sauer in "Organic Reactions," R. Adams, Ed., Vol. 3, John Wiley & Sons, Inc., New York, N. Y., 1946, p 136.

Kinetics of the Nitric Acid Oxidation of Diphenylmethane to Benzophenone[1]

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The mechanism of nitric acid oxidation of diphenylmethane to benzophenone has been kinetically studied with *ca.* 2.5 *M* HNO_3 in 70 vol. % aqueous acetic acid at 90°. The reaction shows an induction period, sodium nitrite being an effective initiator. At the nitrous acid concentration over 0.02 *M*, where the solution is probably saturated with NO_2, the rate is expressed as $v = k[C_6H_5CH_2C_6H_5]$, *i.e.*, the rates are independent of concentrations of nitric and nitrous acids. The *k* value increases with increasing acidity of the media, the plot of log *k vs.* H_0 giving a straight line with a slope of *ca.* −1. A possible mechanism is proposed which involves a rate-determining abstraction of α-hydrogen atom from diphenylmethane by protonated NO_2.

The kinetic studies on the nitric acid oxidation of some substrates, *e.g.*, benzyl alcohol,[2] benzyl ether,[3] and benzaldehyde,[4] have been reported from this laboratory, where aqueous dioxane has been used as a solvent. Dioxane is a suitable solvent, but it may be decomposed by nitric acid, while acetic acid is a stable solvent for oxidation. It is known that diphenylmethane is oxidized to benzophenone by dilute nitric acid,[5] but its mechanism has not yet been reported.

(1) Contribution No 116.

(2) Y. Ogata, Y. Sawaki F. Matsunaga, and H. Tezuka, *Tetrahedron*, **22**, 2655 (1966).

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