7194 J. Am. Chem. Soc. 1986, 108, 7194–7200

The appearance of nitrogen-bearing metal ion products (eq 9d,e) is unexpected and implicates a partial "$NH_2(H_2O)^{-}$" character for the $OH(NH_3)^-$ reactant ion. However, our 4-31+G//4-31G calculations suggest that $[NH_2^-{\cdot}HOH]$ does *not* represent a minimum-energy structure on the proton-transfer potential surface; i.e., $OH(NH_3)^-$ is best represented by a single minimum potential. Therefore, the mechanism for NH_2^- transfer may involve a highly vibrationally excited $OH(NH_3)^-$ cluster ion which is "heated" by the large ion-induced dipole forces accompanying the collision with $Fe(CO)_5$.

Conclusion

In this work we have shown that $Fe(CO)_5$ reacts with a variety of partially solvated negative ions in the gas phase under flowing afterglow conditions at room temperature. Kinetic measurements, product distribution analyses, and thermochemical estimates for these reactions have exposed the following general trends. (i) Most all reactive cluster ions produce an iron tetracarbonyl acyl ion product, $(CO)_4FeC(O)X^-$, from which solvent molecules have been completely expelled. (ii) Compared to the bare ion reactions, addition of the first solvent molecule generally increases the overall efficiency of reaction, while further solvation slows the reaction down. (iii) The overall free-energy changes estimated for the solvated ion reactions with $Fe(CO)_5$ appear to be the best indicators for the occurrence or nonoccurrence of reaction under flowing afterglow conditions. (iv) If the energy of transfer of the negative ion from the cluster to $Fe(CO)_5$ is greater than −34 kcal mol^{-1}, then loss of CO ligands from the metal may accompany solvent expulsion. (v) Products observed in the reaction involving $OH(NH_3)^-$ expose reactive participation of the NH_3 solvent molecule in the ion–molecule encounter involving base-catalyzed decarboxylation of a $(CO)_4\ FeCO_2H^-$ intermediate.

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The Generation of Carbene Anion Radicals from Diazo Compounds. Factors Influencing the Unimolecular Decomposition of the Anion Radicals of Diazo Compounds in Solution

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Abstract: Anion radicals of two diazo compounds, azibenzil and diethyl diazomalonate, had previously been reported to undergo unimolecular decomposition in aprotic solvents to generate the corresponding carbene anion radicals. These processes have been examined in detail by transient electrochemical techniques. The rate constants for the loss of dinitrogen in DMF at 273.2 K are 407 and 125 s^{-1} for the anion radicals of diethyl diazomalonate and azibenzil, respectively. There is little difference in the rate constants in the two solvents. The activation enthalpies fall in the range 10.6–12.7 kcal/mol, and the entropies of activation are close to −6 cal/(K·mol). Hydrogen bonding to water (i) (K_i = 0.8 M^{-1}) facilitates unimolecular decomposition.

$$\mathrm{Ph(PhCO)C{=}N_2^{\bullet-} + HOH/CH_3CN \overset{K_i}{\rightleftarrows} Ph(PhCO)C{=}N_2^{\bullet-}/HOH + CH_3CN} \tag{i}$$

The hydrogen bonded complex, $\mathrm{Ph(PhCO)C{=}N_2^{\bullet-}/HOH}$, undergoes first-order decomposition with a rate constant in acetonitrile at 273.2 K equal to 1700 s^{-1}. This rate enhancement is attributed to the localization of charge away from nitrogen. The carbonyl group adjacent to the diazo function in both substrates also facilitates loss of dinitrogen. It is concluded that unimolecular loss of nitrogen is a more favorable process than previously thought, especially at higher temperatures and when the charge is delocalized.

The thermal decomposition of diazo compounds to yield carbenes is a well-established reaction.[1] Gas-phase studies suggested that diazoalkane anion radicals undergo unimolecular loss of dinitrogen to generate the corresponding carbene anion radicals.[2] Anion radicals of the carbenes, diphenylmethylene and fluorenylidene, have been suggested to be intermediates in the electrochemical reduction of the related diazoalkanes,[3,4] but detailed kinetic studies[5-10] provided powerful evidence to the contrary. Diazodiphenylmethane anion radical does indeed undergo first-order decomposition in acetonitrile and *N,N*-dimethylformamide (DMF). However, solvent deuterium kinetic isotope effects were observed in both solvents implicating reactions of the anion radicals with solvent before irreversible dinitrogen loss takes place.[5,6] The anion radical of 9-diazofluorene undergoes rate-determining dimerization initiating a complex sequence of reactions involving several intermediates before the final product, fluorenone azine, is formed.[9,10] Thus, in these cases more favorable reaction

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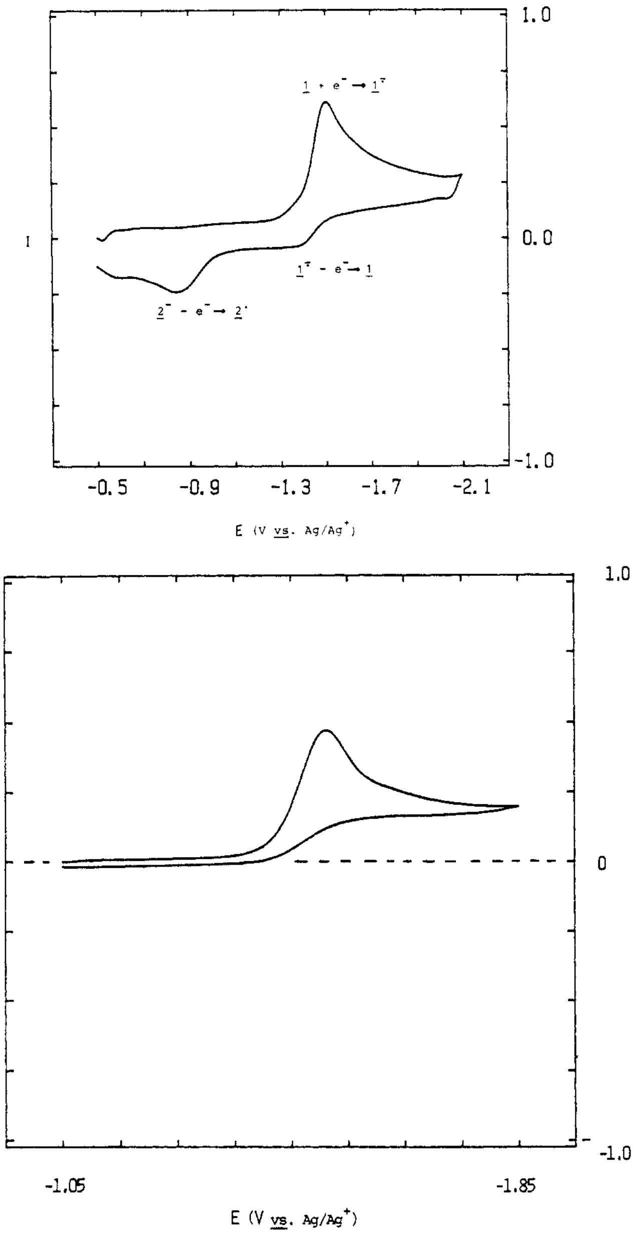
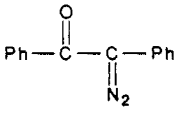


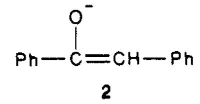
Figure 1. (a) Cyclic voltammogram for the reduction of azibenzil (1.0 mM) in CH_3CN/Et_4NBF_4 (0.1 M) measured at 293 K and 50 V/s. (b) Cyclic voltammogram for the reduction of azibenzil (1.0 mM) in CH_3CN/Et_4NBF_4 (0.1 M) measured at 282 K and 100 mV/s.

pathways exist which have precluded the observation of unimolecular cleavage of dinitrogen.



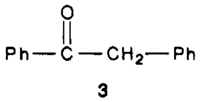
$\mathrm{Ph{-}C({=}O){-}C({=}N_2){-}Ph}$

1



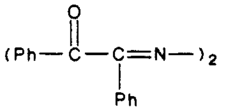
$\mathrm{Ph{-}C(O^-){=}CH{-}Ph}$

2



$\mathrm{Ph{-}C({=}O){-}CH_2{-}Ph}$

3



$\mathrm{(Ph{-}C({=}O){-}C(Ph){=}N{-})_2}$

4

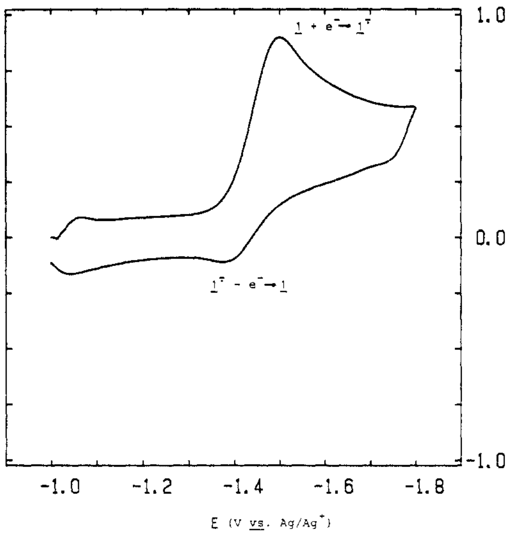


Figure 2. Cyclic voltammogram for the reduction of **1** (1.0 mM) in CH_3CN/Et_4NBF_4 (0.1 M) at 293 K and 100 V/s.

Recently, two independent studies have provided convincing kinetic evidence for the electrochemical generation of carbene anion radicals from the corresponding diazo compounds. In our preliminary communication[11] we presented kinetic evidence that azibenzil (**1**) anion radical undergoes a first-order reaction in acetonitrile to afford the anion **2** as the first detectable product and finally deoxybenzoin (**3**). Under preparative conditions the azine **4** was formed in a competing catalytic process. The absence of a significant solvent deuterium kinetic isotope effect ruled out reaction with solvent as the major reaction pathway. Thus, it was concluded that the rate-determining step in the decomposition is the loss of dinitrogen to give the carbene anion radical. Similarly, Van Galen et al. observed that diethyl diazomalonate (**5**) anion radical undergoes first-order decomposition in either acetonitrile or DMF to produce first the carbanion **6** on the reaction pathway to diethyl malonate (**7**).[12] The first-order kinetics were observed to be independent of solvent and of the presence of several proton donors. A solvent kinetic isotope effect was probed for but not found. It was concluded that the kinetic results were only consistent with initial decomposition to give the carbene anion radical.

$\mathrm{(EtO_2C)_2C{=}N_2}$ **5** $\mathrm{(EtO_2C)_2C\text{-}H^-}$ **6** $\mathrm{(EtO_2C)_2CH_2}$ **7**

A feature that both **1** and **5** have that is absent in diazofluorene and diazodiphenylmethane is a carbonyl group adjacent to the diazo function. This suggests that localization of the charge in the anion radicals to the carbonyl oxygen facilitates the loss of dinitrogen. The purpose of this study was to examine and compare the kinetics of the decomposition of **1**$^{\bullet-}$ and **5**$^{\bullet-}$ in detail. It was hoped that a close examination would provide suggestions as to how carbene anion radicals from other substrates might be prepared. The outstanding feature of the reactions that we find is that they have relatively large activation energies. This suggests that it may be possible to generate carbene anion radicals in other cases simply by conducting the reduction of the diazoalkanes at higher temperatures so that competing processes of lower activation energy may be precluded.

Results

Kinetic Measurements of the Reactions of 1$^{\bullet-}$ in Acetonitrile. The cyclic voltammogram for the reduction of azibenzil measured in CH_3CN/Et_4NBF_4 (0.1 M) at 293 K and a sweep rate of 50 V/s is shown in Figure 1a. The peaks on the return scan are assigned to the oxidation of **1**$^{\bullet-}$ and of **2**$^-$. At a lower sweep rate (0.1 V/s) neither of the oxidation peaks are observed (Figure 1b) indicating complete reaction to form deoxybenzoin (**3**). Under the same conditions at a voltage sweep rate of 100 V/s, the peak due to the oxidation of **1**$^{\bullet-}$ is more pronounced (Figure 2), and the rate constant for the reaction can be derived from the derivative cyclic voltammogram shown in Figure 3. The peak potential separation (Figures 2 and 3) was observed to be equal to 105 mV

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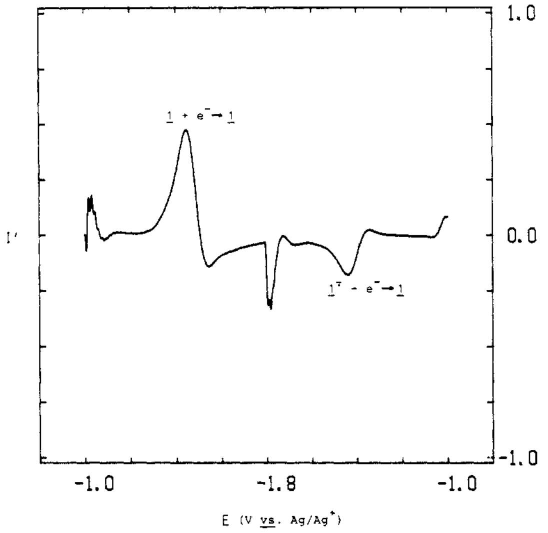

Figure 3. Derivative cyclic voltammogram for the reduction of azibenzil (1.0 mM) in CH_3CN/Et_4NBF_4 (0.1 M) at 293 K and 100 V/s.

Table I. Linear Sweep and Cyclic Voltammetry Data for the Reduction of Azibenzil in Acetonitrile at 281.7 K

[1], mM	$\Delta E^p/\Delta \log \nu$ [a]	$\nu_{1/2}$, Vs^{-1}	k,[b] s^{-1}
0.50	27.5 ± 0.2	79.1	361
1.00	26.0 ± 0.2	85.0	387
2.00	27.5 ± 0.2	78.5	358
4.00	27.9 ± 0.1		
			mean 368 ± 17

[a] In mV/decade. Values are the mean of five replicates for measurements at 0.100 and 1.00 V s^{-1}. [b] Calculated from $\nu_{1/2}$ assuming an eCe_h mechanism.

under the conditions of the measurements indicating quasi-reversible charge transfer.

An indication of the mechanism of the reaction can be derived from the data in Table I. The linear sweep voltammetry slope, ($dE^p/d \log \nu$) where ν is the voltage sweep rate, was observed to be equal to 27.2 mV/decade, in close agreement with the theoretical value (28.1 mV/decade) for a first-order reaction of the anion radical under the conditions of the measurements while E^p was observed to be independent of the substrate concentration. Furthermore, rate constants calculated from DCV measurements, assuming the eCe_h mechanism (eCe_h refers to an overall two-electron process with a homogeneous electron transfer following the rate-determining chemical step), were observed to be independent of the substrate concentration. In the preliminary communication of this work[11] the eCe_h mechanism was favored on the basis of the observation that the current function[13] ($i^p/\nu^{1/2}$) decreased with increasing sweep rate indicating a change in the number of electrons transferred depending upon the extent of reaction. This conclusion is not justified from the peak current experiments for two reasons: (i) quasi-reversible charge transfer and (ii) departure from semi-infinite linear diffusion at low sweep rates by using small electrodes (0.1 mm) could account for a part or all of the observed effect. However, chronoamperometry experiments which are not subject to these effects do indeed show a significant contribution of the eCe_h mechanism (discussed in the following section).

The Arrhenius plot in Figure 4 was constructed by using rate constants derived from DCV data for reactions of $1^{\bullet-}$ in both CH_3CN (*) and CD_3CN (○) over a 40 K temperature range. In both cases the reactions were carried out over neutral alumina[14] to avoid the possible influence of residual water on the results. The Arrhenius activation energy was observed to be 12.3 kcal/mol, and there were no discernible differences between results from the two solutions indicating the absence of a solvent deuterium isotope effect. We attribute the small solvent kinetic isotope effect reported for the low temperatures in our preliminary communications to possible differences in water content in the CH_3CN and CD_3CN. The CD_3CN experiments were carried out over alumina while the CH_3CN experiments were not. The effect of water on observed rate constants is discussed later.

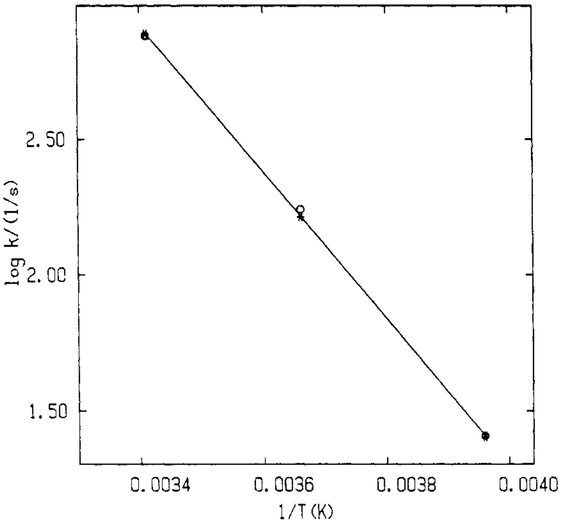

Figure 4. Arrhenius plot for the reactions of $1^{\bullet-}$ in CH_3CN (*) or CD_3CN (○) containing Et_4NBF_4 (0.1 M).

Table II. Double Potential Step Chronoamperometry Data for the Reactions of Azibenzil Anion Radical in Aprotic Solvents

	CH_3CN/Et_4NBF_4 (0.1 M)[a]			DMF/Et_2NBF_4 (0.1 M)[b]		
R_I	τ, ms	I_N	k, s^{-1}	τ, ms	I_N	k, s^{-1}
0.700	1.65	1.000	128	2.07	0.981	102
0.650	2.06	0.995	124	2.36	0.975	108
0.600	2.51	0.990	121	2.69	0.981	112
0.550	3.05	0.995	116	3.10	0.988	114
0.500	3.62	1.000	114	3.54	1.000	116
0.450	4.33	1.005	110	4.11	1.012	115
0.400	5.12	1.010	106	4.74	1.025	115
0.350	5.99	1.025	104	5.49	1.043	114
0.300	7.08	1.040	101	6.43	1.062	112
0.250	8.43	1.055	98.3	7.58	1.080	109
0.200	10.3	1.075	93.7	9.01	1.105	107
			111 ± 11			111 ± 4

[a] Measurements at −15.6 °C. [b] Measurements at −4.5 °C.

Table III. Double Potential Step Chronoamperometry Data for the Reactions of $(EtO_2C)_2C{=}N_2^{\bullet-}$ in Aprotic Solvents

	CH_3CN/Et_4NBF_4 (0.1 M)[a]			DMF/Et_4NBF_4 (0.1 M)[b]		
R_I	τ, ms	I_N	k, s^{-1}	τ, ms	I_N	k, s^{-1}
0.700	1.99	0.989	106	3.38	1.031	62.4
0.650	2.65	0.989	96.1	3.90	1.023	65.4
0.600	3.38	0.989	89.5	4.50	1.015	67.2
0.550	4.15	0.995	85.3	5.13	1.008	69.0
0.500	5.10	1.000	80.6	5.85	1.000	70.2
0.450	6.33	1.017	74.9	6.66	0.992	71.2
0.400	7.60	1.022	71.7	7.59	0.992	71.8
0.350	8.99	1.033	69.5	8.65	0.985	72.2
0.300	10.6	1.044	67.8	9.99	0.988	71.9
0.250	12.5	1.055	66.3	11.6	0.992	71.5
0.200	15.6	1.077	61.9	13.7	0.987	70.5
			79 ± 14			69.4 ± 3

[a] Measurements at −30 °C. [b] Measurements at −24.5 °C.

A Comparison of the Reaction Kinetics for $1^{\bullet-}$ and $5^{\bullet-}$. The heterogeneous rate constant for the reduction of **5** on a glassy carbon electrode at −51 °C was observed to be small giving rise to broad cyclic voltammetry peaks with a large separation between the peaks for oxidation and reduction.[12] By using a mercury

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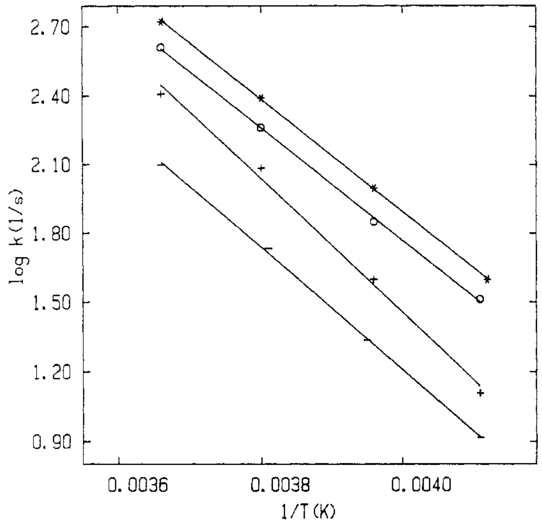

Figure 5. Arrhenius plots for the reactions of diazocarbonyl anion radicals: (*) $5^{\bullet-}$ in CH_3CN/Et_4NBF_4 (0.1 M), (o) $5^{\bullet-}$ in DMF/Et_4NBF_4 (0.1 M), (+) $1^{\bullet-}$ in CH_3CN/Et_4NBF_4 (0.1 M), and (-) $1^{\bullet-}$ in DMF/Et_4NBF_4 (0.1 M).

Table IV. A Comparison of Rate and Activation Parameters for the Reactions of the Anion Radicals in Aprotic Solvents[a]

reactant	solvent	k_{273}, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(K·mol)
$(EtO_2C)_2C{=}N_2^{\bullet-}$	CH_3CN	528	10.6	-6.9
$(EtO_2C)C{=}N_2^{\bullet-}$	DMF	407	10.6	-7.4
$Ph(PhCO)C{=}N_2^{\bullet-}$	CH_3CN	225 (110)[b]	12.7	-0.7 (-4.5)[b]
$Ph(PhCO)C{=}N_2^{\bullet-}$	DMF	125	11.5	-6.4

[a] Measurements by DPSC in the temperature range 243-273 K. [b] On the basis of the theoretical data for the eCe_h mechanism; all other rate constants assume the eC mechanism.

electrode we find that the peak separation is decreased somewhat, but that the charge transfer remains slow. For this reason, it was more suitable to use double potential step chronoamperometry (DPSC) to study the reaction kinetics. DPSC is generally not affected by charge-transfer kinetics since it is usually possible to make potential steps sufficiently large so that charge transfer takes place at diffusion controlled rates in both direction.

The data in Tables II and III were obtained by DPSC measurements on the reactions of $1^{\bullet-}$ (Table II) and $5^{\bullet-}$ (Table III) in both CH_3CN and DMF. The columns labeled R_I are the normalized current ratios, equal to $i(b)/i(f)(0.2929)$, and those labeled τ refer to the potential step length for the appropriate R_I. The heading I_N refers to the quantity, $i(f)t^{1/2}$, normalized so that I_N is equal to 1.000 when $R_I = 0.500$.[15] The theoretical values of I_N from R_I equal to 0.700–0.200 are 1.000 over the entire range for the eC mechanism and 0.936–1.149 for the eCe_h mechanism. The deviation of I_N from unity is in line with expectation if there were a substantial contribution from the eCe_h mechanism. Obviously, the data do not give an exact fit to the theoretical data for either mechanism, but in all cases the fit to the eC theoretical data is the better. Therefore, the rate constants given were calculated from theoretical data for the eC mechanism.

Arrhenius plots for the reactions of both anion radicals in acetonitrile and DMF are shown in Figure 5. The rate constants were evaluated by DPSC, assuming the eC mechanism, at $R_I = 0.500$. Rate constants measured at 273.2 K along with activation parameters for all the reactions are gathered in Table IV. The values given in parentheses for $1^{\bullet-}$ in acetonitrile assume the eCe_h mechanism.

The Effect of Water on the Rate of Reaction of $1^{\bullet-}$ in Acetonitrile. Some difficulty was encountered in attempting to reproduce rate constants obtained in different solvent–electrolyte solutions. It was suspected that the differences observed might be due to differences in the concentrations of residual water in the solutions. To test this, $\nu_{1/2}$ the voltage sweep rate necessary for R_I' to equal 0.500 was measured as a function of the added water (both H_2O and D_2O) concentration in CH_3CN. Since $\nu_{1/2}$ is proportional to the rate constant of the follow-up reaction,[16] the existence of a kinetic isotope effect as well as the reaction order in water could be demonstrated. The results are shown in Table V. The result at zero water concentration refers to measurements in which neutral alumina was added to the cell containing CH_3CN/Et_4NBF_4 (0.1 M). We estimate $[H_2O]$ in electrolyte solutions containing active alumina to be considerably less than 1.0 mM. It has been shown under similar conditions that hydrocarbon dications and dianions, which are extremely reactive toward water, can be observed by slow sweep cyclic voltammetry.[14] Addition of water causes $\nu_{1/2}$ to increase nearly linearly with $[H_2O]$ but with some deviation from linearity at the highest water concentrations. The enhancement of the reaction rate is thus roughly first order in water and shows a modest kinetic isotope effect ($k_H/k_D = 1.25$ at 273.2 K).

Table V. Kinetic Data for the Water Catalyzed Decomposition of $Ph(PhCO)C{=}N_2^{\bullet-}$ in Acetonitrile

$[H_2O]$, M	$(\nu_{1/2}/Vs^{-1})_{H_2O}$	$(\nu_{1/2}/Vs^{-1})_{D_2O}$	$(k_H/k_D)_{app}$[a]	$(k_H/k_D)_{calcd}$[b]
0	34.1			
0.037	44.0	43.2	1.08	1.09
0.074	52.3	49.3	1.20	1.15
0.148	72.0	63.0	1.31	1.22
0.296	109	93.5	1.26	1.26
0.592	167	144	1.21	1.27
			1.25 ± 0.05[c]	

[a] The apparent kinetic isotope effect equal to $(\nu_{1/2})_{H_2O}/(\nu_{1/2})_{D_2O}$. [b] Values calculated by using (6) assuming $(K)_H/(K)_D$ equal to 1.55. [c] The value at $[H_2O]$ = 0.037 M was excluded in the mean.

Table VI. Determination of the Equilibrium Constant for the Association of $Ph(PhCO){=}N_2^{\bullet-}$ with Water in Acetonitrile

$[H_2O]$, M	ΔE^p, mV[a]	K,[b] M^{-1}
0.037	0	
0.368	4.9	0.63
0.731	9.7	0.70
1.09	15.4	0.85
1.44	18.6	0.83
2.14	24.5	0.86
		0.81 ± 0.07[c]

[a] The difference in peak potential measured at 100 V/s and 273.2 K before and after addition of water. Measurements in solvent containing Et_4NBF_4 (0.1 M) at a mercury electrode. [b] Calculated by using (2). [c] The datum for $[H_2O]$ = 0.368 M omitted in the mean.

The Equilibrium Constant for the Association of $1^{\bullet-}$ with Water. The hydrogen bonding equilibrium (1) was studied by the effect of water concentration on the electrode peak potentials measured at 100 V/s and 273.2 K. Attempts to make reversible potential

$$1^{\bullet-} + HOH/CH_3CN \overset{K_{HOH}}{\rightleftharpoons} 1^{\bullet-}/HOH + CH_3CN \qquad (1)$$

measurements by a more precise technique, phase-sensitive second-harmonic ac voltammetry, failed due to deformation in the response. Hydrogen bonding equilibria of a number of anion radicals in aprotic solvents have been determined by reversible potential measurements.[17] The equilibrium constant, K_{H_2O}, was evaluated by using (2) assuming that the peak potentials are

$$K_{H_2O} = (\exp(\Delta E_{rev}/(RT/F)) - 1)/[H_2O] \qquad (2)$$

directly proportional to the reversible potentials, E_{rev}. The equilibrium constant evaluated with $[H_2O]$ ranging from 0.73 to

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Table VII. Apparent *n* Values for the Reduction of Diazo Compounds in Aprotic Solvents

substrate	T, °C	n_{app}	
		CH_3CN^a	DMF^b
$Ph(PhCO)C{=}N_2$	20	1.37	$(1.4)^c$
	0	1.51	$(1.4)^c$
	−20	1.57	$(1.3)^c$
$(EtO_2C)_2C{=}N_2$	20	1.49	1.0
	0	1.38	1.0
	−20	1.46	1.0

[a] The values of $it^{1/2}$ at 95–100 ms during chronoamperometry experiments divided by those obtained in the presence of phenol (10 mM). [b] Obtained by chronoamperometry at 95–100 ms. For $(EtO_2C)_2C{=}N_2$, $it^{1/2}$ was constant after about 3 ms. [c] Obtained by dividing $it^{1/2}$ by 1.2, the estimated square root of the diffusion coefficient ratio for the two substrates, and then dividing by $it^{1/2}$ for reduction of $(EtO_2C)_2C{=}N_2$.

2.14 M was observed to be equal to 0.81 ± 0.07 M^{-1} (Table VI).

The peak potentials measured at 100 V/s are affected by quasi-reversible charge-transfer kinetics. Thus, small corrections could be applied to ΔE_{rev} to take this into account and make (2) rigorously applicable to the data if the parameters for heterogeneous charge transfer were known precisely. However, since these data are not available and there is some scatter in the experimental data, such a correction was not feasible. Since there does not appear to be a trend in the calculated equilibrium constants, we conclude that the heterogeneous charge-transfer contribution to (2) is negligible within the experimental accuracy of the data in Table VI. The treatment of the LSV data in Table I is also subject to quasi-reversible charge-transfer kinetic problems. However, *in that case the voltage sweep rate was 1.0 V/s or less, and under* these conditions the effect is expected to be of minor importance.

The Number of Electrons Involved in the Reduction of 1 and 5. The I_N values in Tables II and III indicate that at τ greater than necessary for $R_I = 0.500$ the number of electrons consumed is greater than 1 in all cases except for the reduction of **5** in DMF. It had previously been shown that a coulometric value of 1 is associated with the latter process.[12] Coulometry studies of the reduction of **1** do not give information about the primary reactions since under preparative conditions a competing catalytic process takes place accompanied by the formation of **4** and results in the consumption of less than 1 Faraday/mol. To obtain additional information on the number of electrons consumed chronoamperometry experiments were carried out in which current-time curves were recorded from 1 to 100 ms at 20, 0, and −20 °C. The data are summarized in Table VII. The addition of phenol (10 mM) to the acetonitrile solutions resulted in very rapid reactions of the anion radicals and the consumption of 2 Faradays/mol. This reaction was used as the basis for determining the number of electrons transferred (n_{app}) in the acetonitrile experiments. The n_{app} listed for acetonitrile solutions were calculated from $it^{1/2}$, which is expected to be proportional to n (the number of Faradays/mol) according to the Cottrell equation,[18] by using (3). In (3)

$$n_{\text{app}} = 2(it^{1/2})/(it^{1/2})_{\text{PhOH}} \tag{3}$$

$(it^{1/2})_{\text{PhOH}}$ is the value obtained in the presence of phenol, and the factor 2 accounts for the fact that the reduction involves 2 Faradays/mol with phenol present. Since $it^{1/2}$ varies with time for the eCe_h mechanism but not the eC mechanism, it was desirable to compare the values at relatively long times where the reaction is essentially complete so that the ratio obtained reflects the deviations from either or both of the two mechanisms. This was accomplished by averaging values obtained between 95 and 100 ms. In DMF solutions $it^{1/2}$ for the reduction of **5** were observed to be constant at times greater than about 3 ms which is the expected result for the eC process. The addition of phenol had little effect on the reaction rates in DMF. The *n* values listed for DMF are based on the constant $it^{1/2}$ for the reduction of **5**, and those for reduction of **1** were obtained by using (4). The

Table VIII. Effect of Supporting Electrolyte Cation on the Relative Rate Constants for Loss of Dinitrogen

R_4NBF_4	$[R_4NBF_4]$, M	$k_{\text{rel}}{}^a$
Me_4NBF_4	$\sim 0.07^b$	2.78
Et_4NBF_4	0.10	1.81
Pr_4NBF_4	0.10	1.53
Bu_4NBF_4	0.10	1.00

[a] Measurements of $\nu_{0\,3}$ in acetonitrile at 293 K. [b] Saturated solution.

$$n_{\text{app}} = (it^{1/2})_{\mathbf{1}}/1.2(it^{1/2})_{\mathbf{5}} \tag{4}$$

subscripts refer to the substrates, and the factor 1.2 is an estimate of the relative diffusion coefficients obtained for the reactions in acetonitrile in the presence of phenol. Since this procedure is uncertain, the n_{app} for **1** in DMF are in parentheses to reflect the uncertainties.

The Origin of the Benzylic Hydrogen in (2). Preparative electrolyses of **1** gave as principal isolated products **4** and **3**, the azine **4** resulting from a catalytic process which competes with the reduction of **1** to **2**.[19a] The catalytic reaction occurs by attack of **2** on **1** and is believed to involve rate-limiting hydride ion transfer from an initial adduct to a further molecule of **1** yielding **4** and, after loss of dinitrogen, regenerating **2**. This conclusion is based on the observation of a substantial kinetic isotope effect when the hydrogen attached to the anionic carbon in preformed **2** is replaced by deuterium.[19b] The product ratio **4**:**3** is not changed when electroreduction of **1** is carried out in CD_3CN instead of in CH_3CN, indicating that the solvent is not the source of the α-hydrogen in **2**. The only other hydrogen source available, aside from residual water, is Et_4N^+, and since this is present in large excess over the substrate, it is conceivable that it reacts with the carbene anion radical in a proton-transfer process. This possibility was regarded as unlikely since in related cases[20a] acetonitrile appears to be a better proton source than tetraalkylammonium ions in reactions with highly basic species such as organic dianions. Although the pK_a of Et_4N^+ is not known, that of Me_4N^+ has been estimated to be equal to 33 (MSAD scale)[20b] which does support this observation. The direct reaction of $\mathbf{1}^{\bullet-}$ with proton donors present in the solvent–electrolyte is ruled out by the observation that substantial amounts of water (a much better proton donor than either acetonitrile or Et_4N^+) must be added in order to enhance the rate of decomposition even modestly. Residual water appears to be the most likely source of benzylic hydrogen arising from non-hydrogen atom abstraction pathways.

The Effect of the Nature and Concentration of Tetraalkylammonium Ions on the Reaction Rate. Although we did not consider it likely, the data presented so far do not rule out the possibility that the anion radicals abstract hydrogen from Et_4N^+ before nitrogen is lost. (This possibility was suggested by a referee.) To test for this, a series of DCV experiments were carried out by using Me_4N^+, Et_4N^+, Pr_4N^+, and Bu_4N^+ as the electrolyte counter ion. The relative rate constants were observed to decrease with increasing size of the tetraalkylammonium ion (Table VIII). If the R_4N^+ were acting as hydrogen atom donors to $\mathbf{1}^{\bullet-}$, the opposite order of reactivity is expected, i.e., Me_4N^+ is expected to be the poorest H atom source. The concentration of Pr_4NBF_4 in acetonitrile was also varied from 0.05 to 0.20 M, and about a 10% decrease in the apparent rate constant was observed with increasing salt concentration. Here again, the observed trend is small and in the opposite direction predicted for hydrogen atom abstraction by $\mathbf{1}^{\bullet-}$ from the Pr_4N^+.

Discussion

Mechanistic Considerations. Although our results on the cathodic reduction of azibenzil (**1**) are less complete in DMF as

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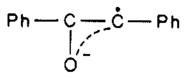
solvent than they are in CH_3CN, all our findings are consistent with a single mechanism, namely, unimolecular loss of dinitrogen from $\mathbf{1}^{\bullet-}$ to give the corresponding carbene anion radical (= the conjugate base of a hydroxyvinyl radical). The evidence comprises the following observations: (i) The product of the heterogeneous reaction at the electrode, the anion radical of azibenzil, $\mathbf{1}^{\bullet-}$, is sufficiently long-lived to permit kinetic analysis of its reactions. (ii) The initial follow-up reaction of $\mathbf{1}^{\bullet-}$ yields the anion of deoxybenzoin (**2**) as the only product. (iii) The follow-up reaction of $\mathbf{1}^{\bullet-}$ is first order and shows no solvent deuterium kinetic isotope effect. (iv) The activation parameters for the follow-up reaction are quite different from those observed for reactions of anion radicals of 9-diazofluorene or diazodiphenylmethane in CH_3CN which respectively dimerize or react with solvent in bimolecular processes; thus for $\mathbf{1}^{\bullet-}$ a much higher value of $\Delta H^{\ddagger}$ is found, and $\Delta S^{\ddagger}$ is much less negative (see below). We believe this evidence for unimolecular loss of dinitrogen from $\mathbf{1}^{\bullet-}$ to be overwhelming, and the case for the formation of the carbene anion radical **8** to be unequivocal.



8

The carbene anion radical **8**, in either CH_3CN or DMF, most likely partitions between hydrogen atom transfer (from solvent or Et_4N^+, or both) and proton transfer from residual water, always present in excess. The branching of the mechanism to include both hydrogen atom and proton transfer is necessary to account for the fact that the overall result is neither purely eC (H atom transfer) nor eCe_h (proton transfer followed by electron transfer) as is evident from the data in Table VII. (The C step in both eC and eCe_h schemes is the loss of dinitrogen. The branching in the mechanism takes place after the rate-determining step.) This reaction pathway has been implicated for the reactions of $(EtO_2C)_2C^{\bullet-}$ in DMF by the effect of proton donors, which do not affect the reaction rate, or the apparent number of electrons transferred.[12]

For purposes of comparison of kinetic and activation parameters we felt it desirable to extend the study of van Galen et al.[12] to the temperature range of our experiments. Necessarily, our examination of the cathodic reduction of diethyl diazomalonate (**5**) has been much less comprehensive than our studies on **1**. All our results are consistent with the earlier findings,[12] and we concur with their conclusion that here too unimolecular loss of dinitrogen from $\mathbf{5}^{\bullet-}$ is the limiting step in the follow-up reaction.

Effects of Protic Additives. Addition of molecules to the reaction system that are more potent proton donors than the solvent or quaternary ammonium ions of the supporting electrolyte accelerate the disappearance of $\mathbf{1}^{\bullet-}$. With added phenol the rate increase is dramatic and is accompanied by a sharp increase in the chronoamperometric current consistent with direct proton transfer to $\mathbf{1}^{\bullet-}$ and an overall two-electron process. In the case of added water the rate increase is not so marked, and at high scan rates the shift in E^p with increasing $[H_2O]$ permits the association constant (0.81 ± 0.07 M^{-1}) to be evaluated.

Two questions arise: (i) What is the nature of the association complex, and (ii) what is the mechanism of the reaction of the complex?

Complexation by hydrogen bonding between water and a number of anion radicals has been demonstrated to occur in aprotic solvents.[17,21] Hydrogen bonding could occur either to the diazo function or to the carbonyl group. Some years ago Pecile et al.,[22] on the basis of infrared studies in mixed aprotic plus hydroxylic solvents, concluded that hydrogen bonding to the carbonyl group of **1** alters the cis/trans rotamer population. Diazoalkanes, for example, $Ph_2C{=}N_2$, do not show hydrogen-bonding effects in their infrared spectra.[23] The anion radical $\mathbf{1}^{\bullet-}$ complexes with water even more strongly than **1** itself so that reaction 1, which involves breaking the hydrogen bond between water and the solvent, is relatively favorable. The dissipation of the negative charge accompanying hydrogen bonding to $\mathbf{1}^{\bullet-}$ might be anticipated to promote loss of dinitrogen since the complex would have increased neutral radical character (see below).

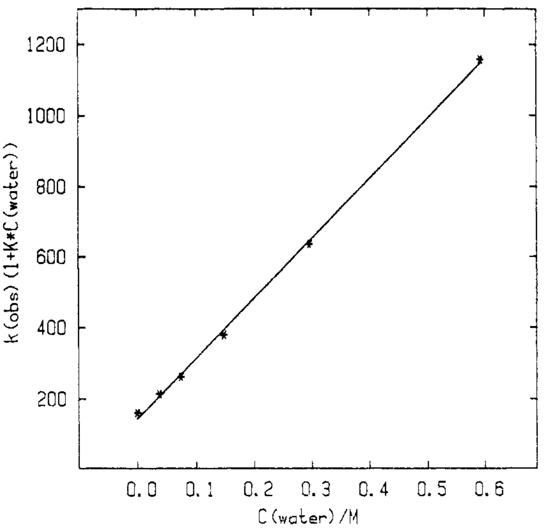


Figure 6. The effect of water on the rate of decomposition of $\mathbf{1}^{\bullet-}$. The k_{obsd} were calculated assuming the eCe_h mechanism.

The observation of the formation of a discrete complex, $\mathbf{1}^{\bullet-}$/HOH, suggests that the appropriate kinetic scheme would be that shown in (5). The observed kinetic coefficient should be given

$$\begin{tikzcd} 1^{\bullet-} + \text{HOH/solvent} \arrow[r, shift left, "K"] \arrow[d, "k_1"] & 1^{\bullet-}/\text{HOH} + \text{solvent} \arrow[l, shift left] \arrow[d, "k_2"] \\ \text{products} & \text{products} \end{tikzcd} \qquad (5)$$

by (6) which takes into account that it is the total anion radical concentration that is measured. This suggests that $k_{obsd}(1 +$

$$k_{obsd} = (k_1 + k_2K[H_2O])/(1 + K[H_2O]) \qquad (6)$$

$K[H_2O])$ should be a linear function of $[H_2O]$ as is observed (Figure 6). This plot, which assumes the eCe_h mechanism, provides an estimate of both k_1 (143 s^{-1}) and k_2 (1700 s^{-1}) which indicates an order of magnitude increase in the ease of loss of dinitrogen from the anion radical after complexing with water. It should be emphasized once more that the mechanism of the reaction is not cleanly eCe_h or eC, and the rate constants are subject to a degree of uncertainty. On the other hand, the mechanistic conclusions can be made from the same type of plot by using the reaction order approach quantity, $\nu_{1/2}$, which does not require the data be compared to a theoretical model.[16] The kinetic deuterium isotope effect on k_{obsd} was evaluated from $\nu_{1/2}$ directly and found to be equal to 1.2 (Table V), rather small to indicate a discrete proton transfer on passing from the complex $\mathbf{1}^{\bullet-}$/HOH to the transition state. It is most likely that the effect is associated with the complexation, i.e., K, since it falls in the range of values previously reported[17,24] for similar hydrogen bonding equilibria of anion radicals in aprotic solvents. By using the values of k_1 and $(K)_H$ determined above and assuming values of $(K)_D$, $(k_{obsd})_H/(k_{obsd})_D$ were calculated at each $[H_2O]$ by using (6). The value of $(K)_D$ giving the best fit between observed and calculated $(k_{obsd})_H/(k_{obsd})_D$ was found when $(K)_H/(K)_D$ was 1.55. These data are included in the last column of Table V.

Comparison of the Reactivity of $\mathbf{1}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ with Related Species. The anion radicals $\mathbf{1}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ show remarkably similar behavior.

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As the results in Table IV show, $\mathbf{5}^{\bullet-}$ is some 4.7 times more reactive than $\mathbf{1}^{\bullet-}$ in CH_3CN at 273 K, the rate factor being somewhat smaller in DMF. The rate differences appear to stem principally from the enthalpy terms, but differences in both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are small. Significantly, $\Delta S^{\ddagger}$ is small and negative in both cases (ca. −6 cal/(K·mol)) where zero or positive values might have been anticipated (for example, loss of dinitrogen from $Ph_2C{=}N_2$ during thermolysis has $\Delta S^{\ddagger} = 0.0$ in CH_3CN[25] and that for thermolysis of 9-diazofluorene in mesitylene is +6.6 cal/(K·mol)[26]). Changes in solvation and/or ion pair interactions could explain this. But it must be kept in mind that $\Delta S^{\ddagger}$, which is normally associated with a rather high degree of uncertainty, is the quantity in which the uncertainty caused by the mixed $eC{-}eCe_h$ behavior will be apparent.

It is instructive to compare the loss of dinitrogen from $\mathbf{1}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ with that from the phenyldiazenyl radical $Ph{-}N_2^{\bullet}$. Brede et al.[27] have reported that at 293 K this reaction takes place in t-BuOH/H_2O (1:1 v/v) with a first-order rate coefficient of 3.4×10^6 s^{-1}. The assumption that $\Delta S^{\ddagger}$ is zero, since the reactant is electrically neutral, leads to $\Delta H^{\ddagger} = 8.4$ kcal/mol, a value not very different from that found here for the reactions of $\mathbf{1}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$. It might be argued that the greater the delocalization of the negative charge in the anion radicals, the closer their structures in the region of the departing nitrogen will resemble $Ph{-}N_2^{\bullet}$. Taking the pK_a value of $RR'CH_2$ as a measure of the ability of the RR′C– moiety in $RR'C{=}N_2^{\bullet-}$ to accommodate the negative charge, it would be predicted that $\mathbf{5}^{\bullet-}$ would react more rapidly than $\mathbf{1}^{\bullet-}$ since **7** (pK_a 15.7 in Me_2SO)[28] is a stronger carbon acid than **3** (pK_a 17.7 in Me_2SO).[29] Notwithstanding this analysis, we feel that such an interpretation on the basis of a small rate difference is probably premature. We note also that rates of thermal decomposition of **1** and **5** have been measured in mesitylene as solvent and **1** is more reactive than **5** by a factor of 15000 at 373 K[26] implying that other structural factors than charge delocalization may be important in controlling dinitrogen loss. Since in the present work we are dealing with charged species the charge factor will be amplified. Significantly $\Delta S^{\ddagger}$ is positive in both the thermolysis of **1** (14 cal/(K·mol)) and **5** (8.6 cal/(K·mol)), but again the rate difference arises mainly from the smaller $\Delta H^{\ddagger}$, 30 kcal/mol for **1**, some 5 kcal/mol less than for **5**.

We conclude that our present observations that the activation parameters for the reactions of $\mathbf{1}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$, $\Delta H^{\ddagger}$ = 10–12 kcal/mol and $\Delta S^{\ddagger}$ = −4.5–7.5 cal/(K·mol), are consistent with unimolecular loss of dinitrogen. The smaller values of $\Delta H^{\ddagger}$ and the larger negative values of $\Delta S^{\ddagger}$ found for the reactions of the anion radicals of 9-diazofluorene and diazodiphenylmethane are clearly quite different and confirm our earlier claim that in CH_3CN the reactions are bimolecular processes (dimerization or reaction with solvent) not involving dinitrogen loss. (The behavior of $Ph_2C{=}N_2^{\bullet-}$ in DMF on this basis is more nearly that which would be expected for unimolecular loss of dinitrogen as was originally proposed by McDonald et al., but the solvent deuterium isotope effect on the rate suggests a bimolecular process. This descrepancy remains to be resolved.) Indeed, we believe that the activation parameters serve as a good guide to mechanism for the reactions of anion radicals of diazo compounds. Since $\Delta H^{\ddagger}$ for unimolecular loss of dinitrogen from anion radicals is intermediate between the high values (ca. 30 kcal/mol) for thermolysis of the parent diazo compounds and the low values for competing bimolecular processes of the anion radicals, we believe that in most cases, at an intermediate temperature unimolecular decomposition of the anion radicals will be detectable providing that measures are taken to make the known competing reactions (i.e., dimerization and reaction with solvent) less favorable. This suggests that a much wider range of carbene anion radical structures will be accessible than thought hitherto.

Experimental Section

Azibenzil (1) was prepared by oxidation of benzil monohydrazone following the procedure of Nenitzescu and Solomonica.[30] It had mp 79–80 °C (lit.[30] 79 °C) and its purity was checked by microanalysis.

Diethyl diazomalonate (5) was prepared by diazo group transfer from tosyl azide to diethyl malonate by the method of Regitz and Liedhegener.[31] The yellow oil produced was spectroscopically and chromatographically pure and crystallized on storage in the refrigerator.

Transient Electrochemical Measurements. The electrodes were constructed from platinum wires (0.1–0.4 mm diameter) embedded in glass and polished to planar surfaces before electrochemically depositing thin layers of mercury. The cells and instrumentation as well as the data handling procedures were the same as those described in previous publications.[32] Data processing was accomplished with an on-line computer.

Reduction of Azibenzil in the Presence of Phenol. Reductions were carried out at a smooth platinum cathode (area 50 cm^2) in a stirred divided cell maintained at 30 °C. Azibenzil (0.25 mmol) and phenol (1.25–12.5 mmol) were dissolved in 75 mL of acetonitrile saturated with Me_4NBF_4. After the passage of a rapid stream of nitrogen for about 15 min, electrolysis was begun at constant current in the range 10–40 mA. Most electrolyses were interrupted after the passage of about 2.5×10^{-4} Faradays, and the electrolyte was then poured into water (500 mL). The mixture was extracted with CH_2Cl_2 (100 mL), and the extract was washed with sodium hydroxide to remove phenol and then with water until the washings were neutral. The extract was dried over Na_2SO_4 and evaporated in vacuo at room temperature. The residue was examined by TLC (by using CH_2Cl_2 + pentane 2:1 v/v) and by HPLC by using μ-Bondapak reverse phase column (octadecylsilane on silica; Waters) by using $CH_3CN{-}H_2O$ (85:15) with UV detection at 254 nm. In all cases the major product was **3** with only a trace of benzil monohydrazone and benzil azine detectable. Unidentified byproducts became detectable in electrolyses carried to >90% conversion of the diazoketone. The apparent n value was determined to be 2.1 Faradays/mol. A typical product distribution at 50% conversion was deoxybenzoin (94%), benzil monohydrazone (2.7%), and benzil azine (2.5%).

Registry No. 1, 3469-17-8; $\mathbf{1}^{\bullet-}$, 104489-69-2; **4**, 3893-33-2; $\mathbf{5}^{\bullet-}$, 93614-14-3; Et_4NBF_4, 429-06-1; Me_4NBF_4, 661-36-9; Pr_4NBF_4, 338-38-5; Bu_4NBF_4, 429-42-5; diethyl diazomalonate, 5256-74-6; water, 7732-18-5; deoxybenzoin, 451-40-1; benzil monohydrazone, 5344-88-7.

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