

the chemoselectivity is governed by adsorption phenomena.

Conclusion. The results presented above demonstrate that a semiconductor catalyst may be photogenerated from a coordination complex and that it is efficiently stabilized in water by addition of an organic compound. In the case of cubic *n*-ZnS, stabilization is linked to catalytic H₂ evolution and chemoselective dehydrodimerization of cyclic ethers. This selectivity may be considered to be due to specific adsorption of the ether onto the ZnS photocatalyst. In addition it was shown that the formation of D₂ does not provide prime evidence for the consumption of water in sa-

crificial hydrogen-producing systems.

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Registry No. 1, 18958-61-7; 2 (isomer 1), 94731-60-9; 3 (isomer 1), 94731-61-0; 3 (isomer 2), 94731-63-2; 4 (isomer 1), 94731-62-1; 4 (isomer 2), 83044-27-3; 2,5-DHF, 1708-29-8; THF, 109-99-9; ZnS, 1314-98-3.

Kinetic Evidence for the Formation of the Carbene Anion Radical (EtO₂C)₂C^{-•}¹

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Abstract: The electrochemical reduction of (EtO₂C)₂C=N₂ (**1**) has been studied in *N,N*-dimethylformamide and acetonitrile at temperatures as low as -64 °C in order to obtain kinetic evidence for the intermediacy of the carbene anion radical (EtO₂C)₂C^{-•}. In the absence of an added proton donor, reaction of the anion radical (I^{-•}) that is formed by the slow, one-electron reduction of **1** obeys the first-order rate law $-d[I^{\cdot-}]/dt = k[I^{\cdot-}]$, where $k = 8 \pm 2 \text{ s}^{-1}$ at -38 °C, and gives (EtO₂C)₂CH⁻ as the principal product. A coulometric *n* value of 1 is obtained for the reduction of **1** in aprotic media. In the presence of an excess of the electroinactive proton donor benzoic acid, guanidinium perchlorate, or (CF₃)₂CHOH, reaction of electrogenerated I^{-•} obeys the first-order rate law $-d[I^{\cdot-}]/dt = 2k[I^{\cdot-}]$, where *k* is the same as that in aprotic media, and affords (EtO₂C)₂CH₂ as the final product. The coulometric *n* value for the reduction of **1** under protic conditions is 2. A scheme is proposed in which the carbene anion radical that is formed by the rate-determining loss of N₂ from I^{-•} undergoes hydrogen-atom abstraction in aprotic media or protonation followed by reduction by unreacted I^{-•} in the presence of an added proton donor.

Dissociative electron attachment to diazoalkanes (R₂C=N₂) has been shown to be a convenient and ready method for the preparation of carbene anion radicals (R₂C^{-•}) in the gas phase.² Whether or not reductive elimination of N₂ from diazoalkanes can be used successfully to prepare carbene anion radicals in the condensed phase is less clear. Our initial claims for the formation of carbene anion radicals^{3,4a} in the condensed phase have been refuted,^{5,6} in part because of our erroneous assignments of the anodic peaks for Ph₂C=N₂^{6,8} and Fl=N₂^{6,8} and Fl=N₂^{6,8} and Fl=N₂^{6,8} (Fl =

9-fluorenylidene)^{4b} to Ph₂CH⁻ and fluorenylidene anion radical, respectively.

Recent demonstrations^{6,8} that several electrogenerated diazoalkane anion radicals can be observed directly at reduced temperature suggest that kinetic studies might be used successfully to demonstrate carbene anion radical intermediacy. In order to focus on the kinetics of the diazoalkane anion radical reaction, we sought a diazoalkane for study that does not afford the corresponding azine as a product. Previous studies of Ph₂C=N₂³ and Fl=N₂^{4a} have shown that azine formation occurs by one or more electron-transfer-induced chain reactions and that the occurrences of these chain reactions greatly increase the complexity of the electrochemical model. Accordingly, we restricted our search for a suitable R₂C^{-•} precursor to those diazoalkanes that give anion radicals which afford hydrocarbons rather than azines as final products and which have relatively low proton and hydrogen-atom affinities. Because these data are unavailable for R₂C=N₂^{-•}, we have used instead as guides the proton affinity for R₂CH⁻ and whether or not R₂C=N₂ forms non-azine products upon photolysis. Diethyl diazomalonate was selected for detailed study because its p*K*_a of 16⁹ is low compared to most methylene carbon acids and because it gives only non-azine products upon photolysis in pentane.¹⁰

Results and Discussion

Cyclic Voltammetry. The cyclic voltammetric reduction of diethyl diazomalonate (**1**) was studied as a function of scan rate, temperature, and effect of added proton donors, solvent, and supporting electrolyte. In the absence of an added proton donor at 22 °C, the cyclic voltammogram at a glassy carbon electrode

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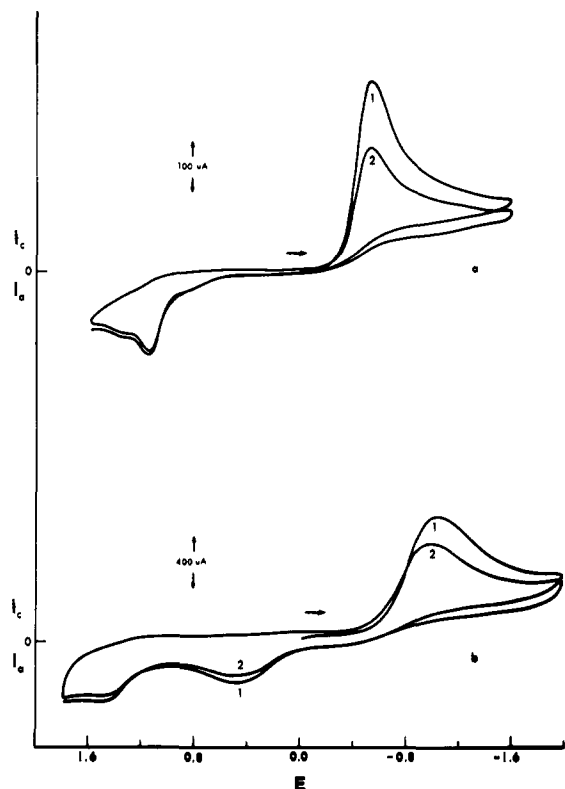
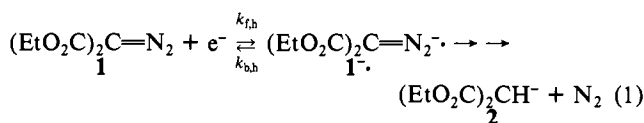


Figure 1. Cyclic voltammograms for the reduction of 8.8 mM **1** in DMF-0.1 M $(n\text{-Bu})_4\text{NClO}_4$ on a glassy carbon electrode: (a) scan rate = 0.2 V/s, $T = 22\text{ }^\circ\text{C}$; (b) scan rate = 10 V/s, $T = -51\text{ }^\circ\text{C}$.

in DMF-0.1 M $(n\text{-Bu})_4\text{NClO}_4$ consists of a single cathodic peak ($E_{p,c} = -0.58\text{ V}$ when $v = 0.2\text{ V/s}$) for the apparent irreversible reduction of **1**, and a single anodic peak at 1.13 V which is due to the irreversible oxidation of a product that arises from the decomposition of I^\cdot (Figure 1a). The assignment (eq 1) of this anodic peak to $(\text{EtO}_2\text{C})_2\text{CH}^\cdot$ (**2**) is based upon the facts that (a) an authentic sample of **2** affords the same redox behavior at all scan rates and temperatures as the electroactive product in question and (b) **2** is the principal electroactive product of the controlled-potential electrolytic reduction of **1** (see coulometry results below). Although no other major process is observed on either



this or any subsequent cycle in the potential range from 1.6 to -2.2 V , two small anodic processes ($E_{p,a} = 0.8\text{ V}$ and $E_{p,a} = 1.3\text{ V}$) are usually discernible as shoulders on the anodic peak for **2** (Figure 1a). Neither of these processes has been identified.

As the temperature is lowered and/or the scan rate is increased, the peaks for **1** and **2** shift in the negative and positive directions, respectively (Figure 1b). These shifts in peak potential are consistent with slow heterogeneous electron transfer.¹¹ In addition, a second major anodic peak emerges near 0.4 V. This peak is linked kinetically to the more positive anodic peak that has been assigned to the oxidation of **2** ($E_{p,a} = 1.4\text{ V}$ when $v = 10\text{ V/s}$ and $T = -51\text{ }^\circ\text{C}$) and increases in relative magnitude at the expense of the anodic peak for **2** as the temperature is lowered or the scan rate is increased.

The assignment of the anodic peak near 0.4 V to the reoxidation of unreacted I^\cdot is based on the results of a recent triple-potential-step chronoamperometry (TPSCA) study.⁸ Although the details of the TPSCA experiment will not be recounted here, basically the experiment involves the measurement of current as

a function of time during each of three potential steps: **1** is reduced to I^\cdot during the first step, the species in question is oxidized during the second step, while **1** is again reduced to I^\cdot during the third step. If it is I^\cdot rather than its reaction product that is oxidized during the second potential step, then the current for the reduction of **1** to I^\cdot during the third potential step will be enhanced proportionately over that expected for the simple diffusion of **1** to the electrode during these steps. The experimental data clearly fit a model in which I^\cdot gives rise to the anodic peak at 0.4 V in Figure 1b and is consumed on the time scale of these experiments in a first-order or pseudo-first-order reaction.

Although the 1.4-V separation between the corresponding cathodic and anodic peaks for $\text{I}^\cdot/\text{I}^\cdot$ is unusually large, significant potential separations between the cyclic voltammetric peaks have also been observed for the chemically reversible redox couples $\text{Ph}_2\text{C}=\text{N}_2/\text{Ph}_2\text{C}=\text{N}_2^\cdot$ ^{6,8} and fluorenone hydrazone/fluorenone hydrazone anion radical.⁸ The origin of this behavior will be discussed below in the section involving the effect of supporting electrolyte.

Double-Potential-Step Chronoamperometric Kinetic Studies of the Reaction of I^\cdot in the Absence of an Added Proton Donor. The results of digital simulation for a first-order chemical reaction subsequent to electron transfer show that the anodic current during the second potential step of the TPSCA experiment is a more sensitive function of the amount of unreacted I^\cdot than the cathodic current during the third potential step.⁸ Accordingly, a two-step method (DPSCA) was used for most of the kinetic studies involving I^\cdot in aprotic media. In the DPSCA technique, the current is measured as a function of time after each of two changes in the electrode potential. Initially, the potential is stepped from a point ($E_{\text{initial}} = 0.0\text{ V}$) where no electrochemical process occurs to a value which is sufficiently negative ($E_1 \leq -1.50\text{ V}$) such that the concentration of **1** at the electrode surface is effectively zero. Control experiments demonstrated that this reduction is diffusion-controlled. After reduction of **1** to I^\cdot has been effected at this potential for time τ , the potential is then stepped to a value ($E_2 = 0.70\text{ V}$) which is sufficiently positive to cause the oxidation of I^\cdot but is insufficiently positive to cause the concurrent oxidation of **2** ($E_{p,a} = 1.4\text{ V}$ when $T = -51\text{ }^\circ\text{C}$). Experimentally, the anodic current that is obtained when $t > \tau$ is divided by the cathodic current at $t = \tau$. When the chemical reaction approaches completion, the decrease in the concentration of unreacted I^\cdot causes the $i_{a,t>\tau}/i_{c,t=\tau}$ current ratio to approach zero.

The rate constant for the reaction of I^\cdot at $-51\text{ }^\circ\text{C}$ in DMF-0.1 M $(n\text{-Bu})_4\text{NClO}_4$ was obtained by fitting the experimental data to dimensionless working curves that were obtained by the digital simulation of an EC process (electron transfer-chemical reaction).¹² As shown in Figure 2, the data give an excellent fit to the several working curves ($(t - \tau)/\tau = 0.2, 0.3, \text{ and } 0.5$) for a follow-up chemical reaction in which the rate law is $-d[\text{I}^\cdot]/dt = k[\text{I}^\cdot]$ and $k = 2.3 \pm 0.4\text{ s}^{-1}$. As required for a first-order or a pseudo-first-order reaction involving I^\cdot , the rate constant is independent of both the concentration of **1** ($2\text{ mM} \leq [\text{1}] \leq 8\text{ mM}$) and the cathodic electrolysis time, τ ($50\text{ ms} \leq \tau \leq 2\text{ s}$). Similar measurements of the rate constant for the reaction of I^\cdot were made with other combinations of temperature, solvent, and electrolyte conditions by both DPSCA and TPSCA (Table I). Within experimental error, all data fit a model in which I^\cdot undergoes a slow, first-order or pseudo-first-order reaction.

Response limitations that are imposed by the electrochemical cell require that $\tau \geq 50\text{ ms}$, while the relatively rapid rate of I^\cdot reaction, even at $-51\text{ }^\circ\text{C}$, sets an effective limit of 2 s for τ_{max} . It should be noted that, although the precision of the data within any one run is generally excellent, problems involving slow heterogeneous electron transfer, uncompensated potential loss between the reference and working electrodes, and the difficulty of excluding background processes at both short τ and very negative applied potentials may create a random error which is 30% or more of the reported rate constant. Generally, this uncertainty increases

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Table I. Kinetic Data for the Reaction of $(EtO_2C)_2C=N_2^-$

entry	solvent, electrolyte	temp, °C	k, s^{-1}			
			absence of H^+ donor ^a		presence of H^+ donor	
			DPSCA	TPSCA	SPSCA ^b	proton donor
1	DMF, TBAP	-51	2.3 ± 0.4	2.4 ± 0.4^c	2.3 ± 0.4	HFIP
2	DMF, TBAP	-51	2.4 ± 0.4	2.6 ± 0.4	2.6 ± 0.4	GP
3	DMF, TBAP	-51			2.6 ± 0.4	C_6H_5COOH
4	DMF, TBAP	-64	0.35 ± 0.05			
5	DMF, TMAPF ₆	-38			8 ± 2	HFIP
6	DMF, TBAP	-38	8 ± 2		8 ± 2	C_6H_5COOH
7	CH_3CN , TBAP	-38	8 ± 2	7 ± 2	7 ± 2	HFIP
8	CD_3CN , TBAP	-38	11 ± 4			

^a (DPSCA) Double- and (TPSCA) triple-potential-step chronoamperometric experiments were conducted in the absence of an added proton donor. ^b Single-potential-step chronoamperometric (SPSCA) experiments were conducted in the presence of an added proton donor ([proton donor]/ $[EtO_2C)_2C=N_2^-] > 10$). GP = guanidinium perchlorate; TBAP = $(n-Bu)_4NClO_4$; TMAPF₆ = $(CH_3)_4NPF_6$, and HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol. ^c Reference 8.

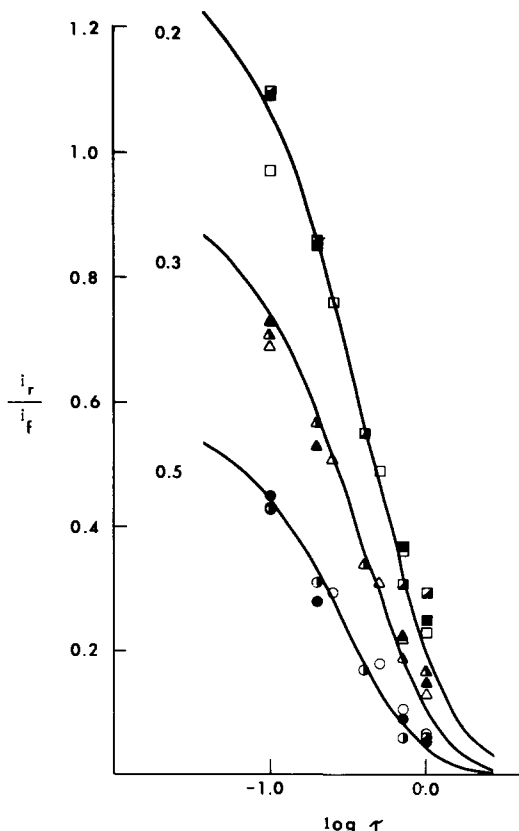


Figure 2. Double-potential-step chronoamperometric data for the reduction of **1** in DMF-0.1 M $(n-Bu)_4NClO_4$ on a planar glassy carbon electrode at -51 °C for $(t - \tau)/\tau = 0.2, 0.3,$ and 0.5 . The solid curves were obtained by the digital simulation of a first-order EC process (Scheme 1) in which $k = 2.5 s^{-1}$. Concentrations of **1**: 2.2 mM (filled symbols), 5.8 mM (half-filled symbols), and 6.1 mM (open symbols).

rapidly when k becomes larger than about $2 s^{-1}$. The value that was obtained for the reaction of 1^- in CD_3CN in three separate runs represents the upper limit for a first-order rate constant that can be studied by the DPSCA method under these conditions with our equipment (entry 8, Table I). The large uncertainties in these rate constant measurements prevent us from determining a solvent isotope effect. Unfortunately, the freezing of acetonitrile solutions precludes experiments at temperatures where the rate constants would be more amenable to study.

Effect of Added Proton Donors. At room temperature, the addition of an excess of $(CF_3)_2CHOH$ (HFIP), an electroinactive proton donor, to a solution of **1** causes the anodic peak for the oxidation of **2** to disappear and the cathodic peak due to the reduction of **1** to double in height. Separate control experiments demonstrated that there is no reaction between **1** and HFIP and that **2**, if it were formed during the reduction of **1** in the presence of HFIP, would be protonated by HFIP to give the conjugate acid

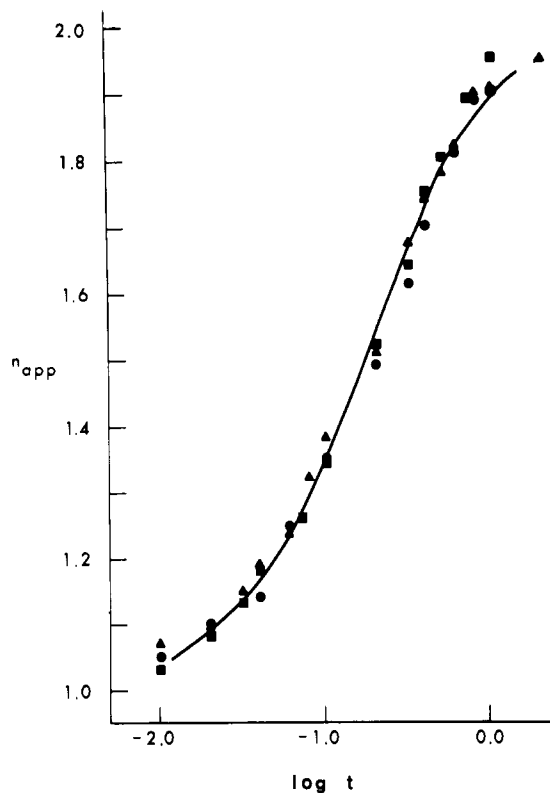


Figure 3. Single-potential-step chronoamperometric data for the reduction of **1** on a planar glassy carbon electrode in DMF-0.1 M $(n-Bu)_4NClO_4$ at -51 °C in the presence of excess HFIP. The solid curve was obtained by the digital simulation of a first-order ECE process (eq 8, 9, and 11) in which $-d[1^-]/dt = 2k[1^-]$ with $k = 2.3 s^{-1}$. Concentrations of **1**: 2.2 mM (\square), 3.8 mM (\blacktriangle), and 5.8 mM (\bullet).

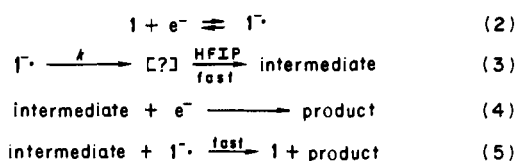
$(EtO_2C)_2CH_2$ (**3**) as an electroinactive product. The chronoamperometric n value of **2** for the reduction of **1** was also diffusion-controlled for $t \geq 20$ ms and was twice the value that was obtained when no proton donor was present.

At -51 °C, the addition of an excess of HFIP causes the ratio of the cyclic voltammetric cathodic peak currents for the reduction of **1** in the presence and absence of the proton donor to approximately double as the scan rate is decreased from 50 to 0.2 V/s. The proton donor again causes the anodic peak assigned to the oxidation of **2** to disappear, but it has no readily discernible effect on the anodic peak assigned to the oxidation of 1^- ($E_{p,a} = 0.4$ V at -51 °C and $v = 10$ V/s).

In order to determine the rate constant of the initial reaction involving 1^- , single-potential-step chronoamperometry (SPSCA) was used to monitor the change in the apparent n value, n_{app} , with increasing time.¹³ At -51 °C, DMF- $(n-Bu)_4NClO_4$, $[HFIP]/[1]$

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Scheme I



$= 10$, and $E = -1.50$ V, n_{app} for the reduction of **1** increases smoothly from a lower limit of 1 when $t < 5$ ms to an upper limit of 2 when $t > 2$ s (Figure 3). In addition, the rate of reaction of 1^- does not change when $[\text{HFIP}]/[\mathbf{1}]$ is increased from 10 to 20. This result demonstrates that the proton donor is not involved in the rate-determining step for the reaction of 1^- .

A kinetically controlled chronoamperometric n value that increases smoothly from a lower limit of 1 for small values of t to an upper limit of 2 for large values of t is consistent with either the ECE process (electron transfer–chemical reaction–electron transfer) described by eq 2–4 or the ECE process described by eq 2, 3, and 5 (Scheme I).¹³ Since HFIP causes the limiting chronoamperometric n value to be double that in the absence of the proton donor, HFIP must react (eq 3) rapidly with a short-lived intermediate that is formed subsequent to the rate-determining step to produce a reducible intermediate. Although both ECE processes would afford the same product in an overall two-electron reaction, the distinction between the two processes is whether the electroactive intermediate that is formed in reaction 3 is reduced at the electrode surface (eq 4) or is reduced by unreacted 1^- (eq 5) in bulk solution.

All results point to the reduction of the reducible intermediate by unreacted 1^- (eq 5). First, because 1^- has some stability on the time scale of these electrochemical experiments at -51 °C, decomposition of 1^- and the formation of the reducible intermediate must occur in bulk solution rather than at the electrode surface. Thus, if this intermediate were to be reduced at the electrode surface, it must both be sufficiently long-lived to diffuse back to the electrode surface and not be reduced by unreacted 1^- . On the basis of the limiting n value of 2 and the formation of $(\text{EtO}_2\text{C})_2\text{CH}_2$ (**3**) (vide infra) as the principal product, the reducible intermediate in question appears to be $(\text{EtO}_2\text{C})_2\text{CH}\cdot$. If this suggestion is correct, then neither of the above requirements should be met. Cyclic voltammetric oxidation of **2**, which presumably affords $(\text{EtO}_2\text{C})_2\text{CH}\cdot$, was shown in separate control experiments not to give a discernible cathodic peak at all scan rates up to 100 V/s at -51 °C in DMF. This result means that the lifetime of $(\text{EtO}_2\text{C})_2\text{CH}\cdot$ must be significantly less than that of 1^- , a species which is observed electrochemically. This result also implies that $(\text{EtO}_2\text{C})_2\text{CH}\cdot$ is incapable of diffusion from the point of its formation in bulk solution to the electrode surface before undergoing chemical reaction. In addition, the difference between the oxidation potential for **2** ($E_{\text{pa}} = 1.13$ V at $v = 0.2$ V/s and room temperature) and the reduction potential for **1** ($E_{\text{pc}} = -0.58$ V) indicates that reduction of $(\text{EtO}_2\text{C})_2\text{CH}\cdot$ by unreacted 1^- is readily feasible thermodynamically.

Second, the rate law $-d[1^-]/dt = k[1^-]$ should be applicable if reduction of the electroactive intermediate occurs at the electrode surface (eq 4), whereas the rate law $-d[1^-]/dt = 2k[1^-]$ must hold if the electroactive intermediate is reduced rapidly by unreacted 1^- in bulk solution (eq 5). The necessity of including the integer 2 in the rate law for the reaction of 1^- when a proton donor is present and the limiting chronoamperometric n value of 2 when kt is large are the result of the consumption and regeneration of one molecule of 1^- and **1**, respectively, by the rapid homogeneous electron-transfer reaction (eq 5). Distinction between these rate laws can be made because HFIP has been shown above not to be involved in the rate-determining step of the reaction for 1^- . This result requires that the same first-order rate constant must be obtained for the rate-determining reaction of 1^- under both aprotic and protic conditions. The experimental data (Figure 3) fit the digitally simulated n_{app} vs. t curve for the reactions described by eq 2, 3, and 5 and afford the same first-order or pseudo-first-order rate constant (2.3 ± 0.4 s⁻¹), when the rate law $-d$

$[1^-]/dt = 2k[1^-]$ is applied, as that which was obtained by the DPSCA and TPSCA techniques in the absence of added proton donor (Table I). This result strongly suggests that the unobserved reducible intermediate which is formed in eq 3 is reduced principally in bulk solution by unreacted 1^- (eq 5).

The fact that the same rate constant is obtained in aprotic and protic media for the reaction of 1^- rules out rate-determining proton abstraction. The additional fact that n is kinetically controlled in protic media and varies monotonically from 1 to 2 with increasing t also rules out most rate-determining hydrogen-atom abstraction processes. If 1^- were to hydrogen-atom abstract from a component of the solvent–electrolyte system, we would normally expect an overall n value of 1 if the solvent- or electrolyte-derived radical were electroinactive and an n value of 2 if the same radical were electroactive. The only plausible way that the addition of a proton donor could then produce the kinetically controlled n -value effect would be for the electroinactive solvent-derived radical to abstract a hydrogen atom from the proton donor so as to produce an electroactive radical derived from the proton donor.¹⁴ In order to test this possibility, chronoamperometric kinetic studies involving electrogenerated 1^- were also conducted in several other combinations of solvent, electrolyte, and proton donor. As shown by the SPSCA results in Table I, there is no discernible effect on the rate constant for the reaction of 1^- as either the proton donor (HFIP, guanidinium perchlorate, or benzoic acid; entries 1–3, Table I) or the supporting electrolyte ($(n\text{-Bu})_4\text{NClO}_4$ or Me_4NPF_6 ; entries 5–6, Table I) is changed. Although the freezing of CH_3CN –0.1 M $(n\text{-Bu})_4\text{NClO}_4$ solutions prevents kinetic studies on this solvent–electrolyte system at -51 °C, results at -38 °C indicate that there is also no appreciable change in the rate constant upon the substitution of DMF with CH_3CN (compare entries 6 and 7, Table I). The C–H bond dissociation energies for these two solvents are reported to be $D^\circ(\text{NCCH}_2\text{-H}) = 92.9 \pm 2.5$,¹⁵ $D^\circ((\text{CH}_3)_2\text{NC(=O)-H}) = 95.3$,¹⁶ and $D^\circ((\text{HC(=O)N(CH}_3)_2\text{-H}) = 85$ kcal/mol.¹⁷ Although the C–H and O–H bond dissociation energies in HFIP and the N–H bond in the guanidinium ion are apparently unknown, H-atom abstraction from benzoic acid ($D^\circ(\text{PhCOO-H}) = 102$ kcal/mol¹⁸ and $D^\circ(\text{HO}_2\text{CC}_6\text{H}_4\text{-H})$ (assumed equal to $D^\circ(\text{C}_6\text{H}_5\text{-H}) = 110.8$ kcal/mol¹⁹) by a solvent-derived radical would be particularly unfavorable thermodynamically. This insensitivity of the rate constant to a change in the hydrogen atom availability from both the proton donor and the solvent eliminates the possibility that an electroactive radical which is derived from the added proton donor might be formed as a short-lived, electroactive intermediate. This leads us to conclude that the rate-determining reaction for 1^- cannot involve carbon–hydrogen bond formation.

Coulometry and Product Studies. The coulometric n values were determined from plots of the cathodic peak heights for the cyclic voltammetric reduction of **1** as a function of the number of electrons added per molecule of **1**. These plots were linear throughout the first 80% of each controlled-potential electrolysis ($E = -0.85$ V) and afforded $n = 1.0$ when the electrolysis of **1** was effected at a platinum cathode in DMF–0.1 M $(n\text{-Bu})_4\text{ClO}_4$ and $n = 2.0$ when the proton donor HFIP was present in excess ($[\text{HFIP}]/[\mathbf{1}] = 20$) and the electrolysis was effected at a glassy carbon electrode in DMF–0.1 M $(n\text{-Bu})_4\text{NClO}_4$. No electroactive product was formed when **1** was electrolyzed in the presence of HFIP. HPLC and GC/MS analyses of the electrolyzed solution indicated that $(\text{EtO}_2\text{C})_2\text{CH}_2$ was formed quantitatively when HFIP was present.

The cyclic voltammetric examination of electrolyzed solutions showed that **2** was the only electroactive product formed in the

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DMF or CH_3CN , protonation of PhC(=O)CPh^- by CH_3CN and the subsequent reduction of PhC(=O)CPhH^- by unreacted $\text{PhC(=O)C(N}_2\text{)Ph}^-$ appears to be the more plausible explanation.

There are at least two possible explanations as to why PhC(=O)CPh^- proton abstracts from CH_3CN whereas $(\text{EtO}_2\text{C})_2\text{C}^-$ hydrogen-atom-abstracts. First, the proton affinity of PhC(=O)CPh^- may be larger than that for $(\text{EtO}_2\text{C})_2\text{C}^-$. Although the pK_a s for the corresponding acids, PhC(=O)CPhH^- and $(\text{EtO}_2\text{C})_2\text{CH}^-$, are unknown, we have estimated them from the pK_a values of **3** and $\text{PhC(=O)CH}_2\text{Ph}$ and the expected differences in the proton affinities between the corresponding carbanions and carbene anion radicals. The $pK_a^{\text{Me}_2\text{SO}}$ ($\text{PhC(=O)CH}_2\text{Ph}$) = 17.4 is estimated from $pK_a^{\text{Me}_2\text{SO}}$ ($\text{PhCH}_2\text{C(=O)CH}_3$) = 19.4, minus the correction of 2 for the replacement of CH_3 in $\text{PhCH}_2\text{C(=O)CH}_3$ by Ph (e.g., the pK_a s of CH_3COCH_3 and PhCOCH_3 are 26.7 and 24.7, respectively);²⁷ $pK_a^{\text{Me}_2\text{SO}}$ ($(\text{EtO}_2\text{C})_2\text{CH}_2$) = 16.0.⁹ The recently measured gas-phase proton affinity of Ph_2CH^- (PA = 382 ± 2 kcal/mol)²⁸ is 17 kcal/mol greater than that of Ph_2CH^- (PA = 364.5 ± 2 kcal/mol).²⁹ Since the structures and relative energetics in the $\text{Ph}_2\text{CH}^-/\text{Ph}_2\text{C}^-$ pair should be similar to those for $\text{PhC(=O)CHPh}^-/\text{PhC(=O)CPh}^-$, a pK_a for PhC(=O)CHPh^- in the range of 25–31 in the dipolar, aprotic solvent CH_3CN is reasonable. Even though the equilibrium constant for proton transfer from CH_3CN ($pK_a = 31$)²⁷ to PhC(=O)CPh^- most probably will be less than unity, proton transfer can still proceed rapidly if PhC(=O)CHPh^- is rapidly reduced by unreacted $\text{PhC(=O)C(N}_2\text{)Ph}^-$. This latter electron-transfer reaction should be feasible thermodynamically and should proceed rapidly, as in the case of $(\text{EtO}_2\text{C})_2\text{CH}^-/1^-$ (see eq 10).

The failure of $(\text{EtO}_2\text{C})_2\text{C}^-$ to abstract a proton from CH_3CN could be due to the slightly greater acidity of $(\text{EtO}_2\text{C})_2\text{CH}_2$ than $\text{PhC(=O)CH}_2\text{Ph}$ ($pK_a = 16$ vs. $pK_a = 17.4$, vide supra) and a smaller difference in proton affinities for $(\text{EtO}_2\text{C})_2\text{CH}^-/(\text{EtO}_2\text{C})_2\text{C}^-$ than for $\text{PhC(=O)CHPh}^-/\text{PhC(=O)CPh}^-$. The combined effects may be sufficient to render proton abstraction by $(\text{EtO}_2\text{C})_2\text{C}^-$ from CH_3CN unimportant relative to other competing reactions.

The second possible explanation for the difference in behavior for the two carbene anion radicals is based on the rate of hydrogen-atom abstraction that may be significantly greater for $(\text{EtO}_2\text{C})_2\text{C}^-$ than that for PhC(=O)CPh^- . This suggestion comes from consideration of the structures of R_2C^- intermediates. Starting with the calculated ground-state structure of H_2C^- as a $\sigma^2\text{p}^1$ species with an H–C–H angle of 100° ,^{2b} the substitution of the hydrogens by carbonyl and phenyl groups should open this angle somewhat to approach sp^2 hybridization. One of the CO_2Et in $(\text{EtO}_2\text{C})_2\text{C}^-$ and the C(=O)Ph in PhC(=O)CPh^- should overlap the doubly occupied σ orbital of the respective carbene anion radicals. This leaves the other groups, CO_2Et in $(\text{EtO}_2\text{C})_2\text{C}^-$ and Ph in PhC(=O)CPh^- , to interact with the singly occupied carbon p orbital. Thus, it is reasonable to conclude from $D^\circ(\text{CH}_3\text{C(=O)CH}_2\text{-H}) = 98 \pm 2.6$ kcal/mol²⁹ and $D^\circ(\text{PhCH}_2\text{-H}) = 85 \pm 1$ kcal/mol²⁹ that $(\text{EtO}_2\text{C})_2\text{C}^-$ would abstract a hydrogen atom from the solvent ($D^\circ(\text{CH}_3\text{CN}) = 92.9 \pm 2.5$)¹⁵ more readily than PhC(=O)CPh^- . This would allow the competing reaction channel of proton abstraction from CH_3CN to predominate for PhC(=O)CPh^- .

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Experimental Section

Instrumentation. Cyclic voltammetric and chronoamperometric experiments were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic potential loss between the reference and working electrodes.³⁰ Control of the potentiostat and the acquisition and processing of the rapid-scan cyclic voltammetric and chronoamperometric data were performed with a laboratory digital computer (ADAC Model 2000, LSI 11/2). The three-electrode potentiostat which was used for the controlled potential electrolysis has been described previously.³¹

Cells, Electrodes, and Electrolysis Procedures. All electrochemical experiments were performed on an all-glass vacuum line. The solvents were transferred into the cell by trap-to-trap distillation. Traces of oxygen, if present, were removed by several freeze–pump–thaw cycles. Helium was used to bring the cell up to atmospheric pressure. A positive pressure of helium was maintained when the reference electrode and compounds were transferred into the cell. Slush baths, which were prepared from liquid nitrogen and the appropriate liquid, were used to maintain the cell at constant, subambient temperature.

All chronoamperometric experiments which were conducted in the absence of an added proton donor were performed on either a planar platinum or a vitreous carbon electrode that had a geometric area of 0.20 cm^2 ; the vitreous carbon planar electrode was used when an added proton donor was present. All potentials listed were measured with respect to a cadmium amalgam that is in contact with a DMF solution which is saturated with both sodium chloride and cadmium chloride (Type A-III).³² The potential of this electrode is -0.75 V vs. SCE. Dual reference electrodes were used in all rapid-scan cyclic voltammetric and chronoamperometric experiments.³³ The second reference electrode, which was a platinum wire in series with a 0.1- μF capacitor, was placed in parallel with the cadmium amalgam electrode.

The progress of a large-scale electrolysis was monitored periodically by cyclic voltammetry. At the conclusion of an electrolysis, the electrolyzed solution was first analyzed for **2** by cyclic voltammetry and then treated in a dry helium atmosphere with an appropriate proton donor in order to protonate all electrogenerated anions. The solution was then analyzed by high-performance liquid chromatography and/or gas chromatography/mass spectrometry.

Chemicals. All chemicals were purchased from commercial sources except for guanidinium perchlorate³⁴ and diethyl diazomalonate.³⁵ The purity of each compound was verified by a melting point determination and/or HPLC. When necessary, further purification was accomplished by standard distillation or recrystallization procedures. Heat- and light-sensitive reagents were refrigerated or stored at 0°C in well-sealed glass bottles. DMF (Burdick & Jackson) was purified in a dry, nitrogen atmosphere by passage through a column of neutral alumina (80–200 mesh, Brockman activity 1, activated at 600°C for 24 h). The solvent was then collected and stored over a mixture of alumina and activated molecular sieves (Davison 4 Å). Acetonitrile (Burdick & Jackson) and its deuterated analogue (Aldrich Chemical Co., 99 atom % D) were purified according to the procedure of Walter and Ramaley, method B.³⁶ This procedure involves four reflux–distillation steps using, successively, anhydrous Al_2Cl_6 , $\text{KMnO}_4/\text{Li}_2\text{CO}_3$, KHSO_4 , and CaH_2 . The purified solvent was then stored over CaH_2 .

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