

is general. Chemical probes establish trends in reactivity and suggest kinetically important transient intermediates while comparison of a series of structurally related molecules is a powerful means of inferring the key factors that control reaction selectivity and energetics. Surface spectroscopies, such as X-ray photoelectron, high-resolution electron energy loss, and near-edge X-ray absorption fine structure, are important in defining the structure and chemical nature of

nonvolatile surface species and in defining the energetics of bond-breaking processes yielding nonvolatile products.

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Registry No. Trimethylene sulfide, 287-27-4; tetrahydrothiophene, 110-01-0; ethanethiol, 75-08-1; 1-propanethiol, 107-03-9; 1-butanethiol, 109-79-5; 1-pentanethiol, 110-66-7; benzenethiol, 108-98-5; molybdenum, 7439-98-7.

In Search of Carbene Ion Radicals in Solution: Reaction Pathways and Reactivity of Ion Radicals of Diazo Compounds

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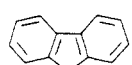
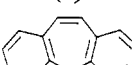
In the period of just over 100 years since the first was prepared,¹ aliphatic diazo compounds, RR'CN₂, have been involved in many important developments in structural organic chemistry, organic synthesis, and the study of organic reaction mechanisms.² A feature of their chemistry is the diversity of reactive intermediates that can be generated by removal of a molecule of nitrogen under various experimental conditions. Perhaps the simplest of such processes is the thermolytic or photolytic cleavage of the C-N bond, which gives rise to carbenes, RR'C:, a field of revitalized activity in recent times.³ Proton transfer to diazo compounds yields diazonium (RR'CHN₂⁺) and carbenium ions (RR'CH⁺), while Lewis acids lead to organometallic analogues. Nitrogen loss by attack of nucleophiles on the diazo function is much less common, but hydride transfer has been reported to give rise to carbanions (RR'CH⁻) in favorable cases.⁴ This Account is concerned with the behavior of diazo compounds in fluid solution when subjected to one-electron reduction or oxidation. For the most part we shall deal with situations in which the initial electron transfer takes place at an electrode, although chemical one-electron oxidizing and reducing agents can also be used.

Aliphatic diazo compounds undergo one-electron oxidation and reduction in solution at readily accessible potentials.⁵ The data in Table I are a representative

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Table I
Redox Potentials of Selected Aliphatic Diazo Compounds RR'CN₂

R	R'	$E_{1/2}(\text{ox})/\text{V}^{a,b}$	$E^p(\text{red})/\text{V}^{a,c}$
H	H	1.70 ^d	
EtO ₂ C	H	2.10 ^d	
EtO ₂ C	EtO ₂ C		-1.33 ^e
EtO ₂ C	Ph	1.43 ^e	
Ph	Ph	0.95 ^d	-1.71 ^h
Ph	PhCO	1.48 ^e	-1.12 (CH ₃ CN) ⁱ
		1.22 ^d	-1.35 ^j
		0.77 ^f	

^a Corrected to SCE. ^b Rotating Pt disk electrode in CH₃CN solution. ^c Cyclic voltammetry on 1-5 mM solutions of the diazo compound in DMF; potential scan rate ca. 100 mV s⁻¹; glassy carbon or Pt working electrode. ^d Reference 6. ^e Reference 7. ^f Reference 8. ^g Reference 9. ^h Reference 10. ⁱ Reference 11. ^j Reference 12.

selection of reported values. It should be remembered that the redox processes to which these potentials refer

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Table II
Structural and Other Information on Methylene Ion Radicals from Theoretical^a and Spectroscopic Studies

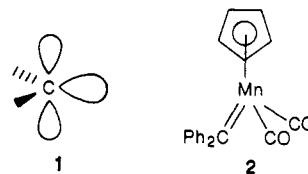
	H_2C^{++} ${}^2\text{A}_1$	$\text{H}_2\text{C}:$		H_2C^{--} ${}^2\text{B}_1$
		${}^3\text{B}_1$	${}^1\text{A}_1$	
$r_{\text{CH}}/\text{\AA}$				
exptl		1.078 ^b	1.111 ^d	
theor	1.093	1.078	1.122	1.140
$\angle\text{HCH}/\text{deg}$				
exptl		136 ± 8 ^b	102.4 ^d	99 ± 3 ^e
theor	136.85	135.80	100.18	99.89
IP/eV				
exptl		10.40 ^c		
theor		9.69	9.31	
EA/eV				
exptl		0.65 ^f	0.25 ^f	
theor		0.39	0.02	

^aTheoretical results are from MNDO/3 calculations,¹³ but these agree closely with values from SCF/CI¹⁴ and ab initio (4-13G) calculations.¹⁵ ^bReference 16. ^cReference 17. ^dReference 18. ^eReference 19. ^fReference 20.

are usually irreversible. The observed potentials are affected by the rate of subsequent chemical processes as well as by slow (heterogeneous) transfer of electrons from the electrode to the diazo compound as is revealed by the dependence of half-wave and peak potentials on potential sweep rate and substrate concentration. The electrochemical irreversibility demonstrates that the ion radicals of diazo compounds are chemically reactive entities. It was our original concern to investigate the possibility that unimolecular loss of dinitrogen might be one of the available reaction pathways for both anion radicals and cation radicals and that the carbene ion radicals so produced might show interesting new patterns of chemical behavior.

There is increasing interest in the structure and chemistry of carbene ion radicals in the gas phase among theoreticians, spectroscopists, and astrophysicists. Table II is a compilation of structural information concerning the parent species H_2C^{++} and H_2C^{--} compared with the neutral carbene in its lowest singlet (${}^1\text{A}_1$) and ground triplet (${}^3\text{B}_1$) state. It is worth noting the similarity in structure between H_2C^{++} (${}^2\text{A}_1$) and the ${}^3\text{B}_1$ state of $\text{H}_2\text{C}:$ and between H_2C^{--} and the ${}^1\text{A}_1$ state of $\text{H}_2\text{C}:$. Experimental data on the methylene ion radicals are largely restricted to the anion but show good agreement with the results of semiempirical and ab initio calculations and are in line with generalizations²² that hydrides with central atoms having formally five valence electrons (H_2C^{++}) will be more nearly linear than those with seven (H_2C^{--}). It should further be noted that removal of an electron from the neutral carbene is energetically much more expensive than

addition of an electron and this suggests that the carbene cation radical will be an exceedingly electrophilic species. With elaboration of the groups attached to the central carbon atom it is to be expected that the structures of both the cation and anion radicals will approximate to 1, with an in-plane sp^2 -type orbital and



an out-of-plane p-type orbital between them accommodating either one or three electrons, but interacting with substituent orbitals of the appropriate symmetry.¹⁹ Information on the behavior of such species in the gas phase is now accumulating from the burgeoning field of gas-phase ion chemistry.²¹

In the liquid phase, the quest for carbene ion radicals has largely concentrated on diazo compounds as precursors and systems in which the central carbon atom is in conjugation with aryl or carbonyl groups. Sargent's studies²³ of the reduction of methylene halides by sodium naphthalene and Vogler's photolysis of the manganese-diphenylcarbene complex 2,²⁴ both thought to lead to carbene anion radical formation, are notable exceptions. The starting point of the search was Webster's²⁵ reduction, both chemical and electrochemical, of tetracyanodiazocyclopentadiene; the production, in protic solvents, of the corresponding cyclopentadienyl anion, and, in the presence of phenol, the occurrence of nuclear substitution led to the suggestion that the carbene anion radical was the key intermediate. On the oxidative side, anodic oxidation of diazomethane in the presence of pyridine gave *N*-methylpyridinium ion and was interpreted on the basis of H_2C^{++} formation.²⁶

In all the early work the evidence for generation of intermediate carbene ion radicals fell short of being totally convincing. The question at issue is one of timing, whether in the transformation of $\text{RR}'\text{CX}^{+/-}$ to product $\text{RR}'\text{CXYZ}$, X^{\cdot} is lost before any further reagent becomes chemically involved. While cases with $\text{X} = \text{N}_2$ are most likely to favor such a situation, the identity of products, alone or in conjunction with indirect kinetic arguments, is insufficient proof; direct studies of the kinetic form of disappearance of the precursors of the putative carbene ion radicals are needed. The quest for carbene ion radicals thus resolved itself into a study of electrochemical kinetics following electron transfer to or from aliphatic diazocompounds at electrodes. It turns out that in general the rates of reaction of the ion radicals of diazo compounds, though fast, are not so fast that the subsequent chemical behavior is affected by the proximity of the electrode surface; the reactions are

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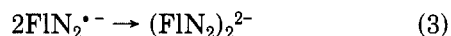
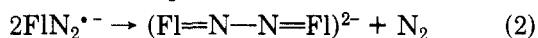
volume reactions rather than surface reactions.²⁷ The situation is much the same as if the diazo ion radicals had been generated from the parent diazo compound by interaction with a chemical one-electron oxidizing or reducing agent in homogeneous solution, except that the initial electron transfer is then often the rate-limiting process and the kinetics of subsequent steps are not directly accessible.²⁸ Aprotic solvents are most generally used so as to minimize proton transfers to $RR'CN_2^{\bullet-}$ or nucleophilic attack on $RR'CN_2^{\bullet+}$, which might facilitate loss of nitrogen and so mask the unimolecular fragmentation that would yield the carbene ion radical. Although other techniques, such as pulse radiolysis,²⁹ have been used, the electrochemical procedures detailed in the next section have given most of the kinetic information, which now reveals a more general picture of the conditions, both structural and environmental, that promote the formation of carbene ion radicals and which permits the delineation of the competing reactions of diazo ion radicals. With the kinetic and mechanistic situation firmly established, the interpretation of the products, their identity, and their proportions can be addressed.

Electrode Kinetic Studies

Reaction of 9-Diazafluorene Anion Radical. The kinetics of the decomposition of 9-diazafluorene anion radical ($FlN_2^{\bullet-}$) in acetonitrile were studied by linear sweep voltammetry (LSV), derivative cyclic voltammetry (DCV), and double potential step chronoamperometry (DPSC).³⁰ The LSV studies allowed an unambiguous assignment of rate law 1 on the basis of

$$\text{rate} = k(FlN_2^{\bullet-})^2 \quad (1)$$

the effect of voltage sweep rate ($dE^p/d \log v$) and the substrate concentration ($dE^p/d \log C_A$) on the electrode peak potential. These studies ruled out unimolecular decomposition to the carbene anion radical as well as the reaction of the anion radical with the substrate as rate-determining steps in the reaction. It was proposed that the initial step in the complex reaction leading to fluorenone azine dianion (eq 2) is the dimerization of the anion radicals to give either a linear or cyclic intermediate dianion (eq 3).



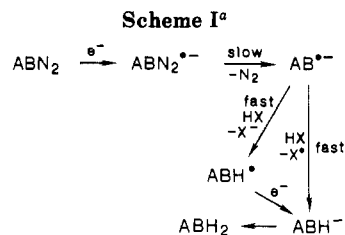
The second-order rate constant for the dimerization was observed to increase with decreasing size of the tetraalkylammonium counterion, ranging from 2.1×10^4 (Bu_4N^+) to 2.1×10^5 (Me_4N^+) $M^{-1} s^{-1}$ at 284 K in acetonitrile.³⁰ The counterion effect on the apparent rate constant was explained on the basis that the degree of ion-pair formation is inversely related to cation size and that ion association enhances the rate of dimerization by decreasing the charge repulsion between the anion radicals in the transition state. This interpretation was supported by the observation of a very low Arrhenius activation energy (2.2 kcal mol⁻¹), indicating a complex mechanism possibly involving a preequilibrium formation of the ion pair.

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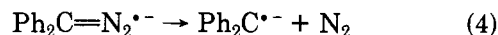
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^aAB = PhCOCHPh.

Decomposition Reactions of Diazodiphenylmethane Anion Radical. Slow charge transfer complicates electrode kinetic studies of the reactions of diazodiphenylmethane anion radical ($Ph_2CN_2^{\bullet-}$) generated in *N,N*-dimethylformamide (DMF) in the presence of Bu_4N^+ ions.³¹ The heterogeneous rate constant was observed to depend strongly on the size of the tetraalkylammonium ion and to be moderately high in acetonitrile in the presence of Me_4N^+ . LSV studies carried out in acetonitrile/ Me_4NBF_4 indicated that the decomposition is first order in the anion radical and independent of the presence of weak proton donors at low concentrations (<20 mM). A DPSC study confirmed the first-order kinetics and yielded a rate constant of about $160 s^{-1}$ at 281 K. These results, taken alone, appear to be consistent with unimolecular decomposition of the anion radical accompanied by the expulsion of dinitrogen (eq 4). However, changing from



CH_3CN to CD_3CN as solvent resulted in a large deuterium kinetic isotope effect, implicating either proton or hydrogen atom abstraction before the loss of dinitrogen.³¹ Hawley's application of triple potential step chronoamperometry to the problem³² subsequently provided confirmatory evidence that eq 4 is not important in cathodic reduction of Ph_2CN_2 .

Unimolecular Decomposition of Anion Radicals of Diazo Compounds. The failure to observe kinetic behavior consistent with the formation of carbene anion radicals during the decomposition of aryldiazoalkane anion radicals led to studies of diazo compounds with carbonyl groups adjacent to the diazo function. In the corresponding anion radical, this structural feature was expected to result in localization of the negative charge on oxygen and to give diazenyl radical character to the nitrogen function. Diazenyl radicals are known to lose dinitrogen readily.

The kinetic behavior of the anion radical of azibenzil (ABN_2) fulfilled expectations.³³ LSV studies in acetonitrile showed that the anion radical decomposes by a first-order mechanism. Use of CD_3CN as solvent resulted in a negligibly small deuterium kinetic isotope effect, ruling out proton or hydrogen atom transfer from the solvent in the rate-determining step. The cyclic voltammogram of ABN_2 showed the presence of only one electroactive product, the carbanion $PhCO\bar{C}HPh$ ($ABH^{\bullet-}$), which was proposed to arise from the reactions shown in Scheme I.

Detailed electrochemical kinetic studies were carried out on the decompositions of the anion radicals of ABN_2

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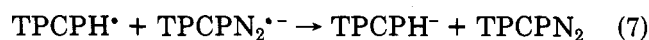
and diethyl diazomalonate in acetonitrile and *N,N*-dimethylformamide.^{9,11} The characteristic features of unimolecular reactions were observed to be (i) first-order kinetics in the absence of proton donors, (ii) increased reactivity in the presence of hydroxylic compounds, which could be accounted for by a pre-equilibrium to produce a more reactive hydrogen-bonded anion radical, (iii) the absence of solvent deuterium kinetic isotope effects, ruling out rate-determining proton or hydrogen atom transfer from the solvent, and (iv) enthalpies of activation of the order of 10–12 kcal mol⁻¹.

Generation of a Hydrocarbon Carbene Anion Radical. Cyclic voltammetry of the reduction of 2,3,4,5-tetraphenyldiazocyclopentadiene (TPCPN₂) indicated that the corresponding anion radical undergoes decomposition to form 2,3,4,5-tetraphenylcyclopentadienyl anion (TPCPH⁻) as the only detectable product.³⁴ DPSC studies revealed that the kinetic behavior of the decomposition parallels that of the anion radicals of ABN₂ and diethyl diazomalonate. Arrhenius activation enthalpies of the order of 13 kcal mol⁻¹ were observed in acetonitrile and DMF.

A further observation of mechanistic interest in this case is that TCPH⁻ is formed in an eC process. This was established by chronoamperometric measurements. This observation implicates hydrogen atom abstraction (5) from solvent (S-H), or other donors, as the pre-

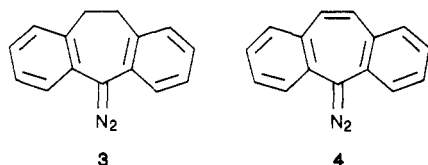


dominant mode of reaction of TCP^{•-}, the carbene anion radical. An alternative pathway (6) involving



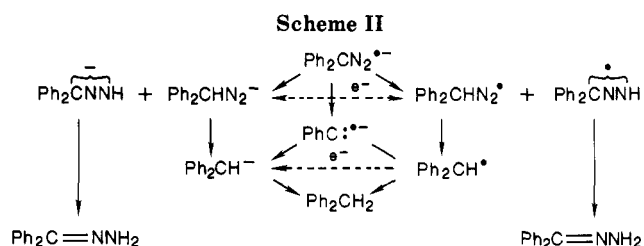
proton transfer from S-H would produce 2,3,4,5-tetraphenylcyclopentadienyl radical (TCPH[•]), which would be expected to acquire an electron by transfer from the substrate anion radical in homogeneous solution (e_h) to generate the final product of the reaction, TCPH⁻ (eq 7), and regenerate substrate (see below).

Kinetics of the Formation of Carbene Cation Radicals from Diazoalkane Cation Radicals. The decomposition reactions of three diazoalkane cation radicals generated from diazodiphenylmethane and the related compounds 3 and 4 were studied in acetonitrile,



methanol, and mixtures of these solvents.³⁵ In the presence of pyridine bases, the proton-catalyzed chain decompositions of the substrates are inhibited³⁶ so that the primary reactions of the cation radicals could be probed.

The outstanding features of the cation radical decompositions were observed to be (i) first-order kinetics independent of the presence and concentrations of nucleophiles (pyridines and methanol) and (ii) Arrhenius activation energies of the order of 16 kcal



mol⁻¹.³⁵ The observed rate constants were very nearly independent of the solvent, and the kinetic isotope effects observed upon changing the solvent from CH₃-OH to CD₃OD were insignificantly small. It was concluded that the observed kinetics are only consistent with unimolecular cleavage of the carbon-to-nitrogen bond in the cation radicals to generate the corresponding carbene cation radicals. The overall reactions are of the eC-eC_eh competition type, giving rise to the consumption of 1–2 F mol⁻¹, depending upon the substrate and conditions. The eC_eh mechanism differs from the eC case in that 2 rather than 1 F mol⁻¹ is consumed.

Product Formation

Methodology. A major problem in understanding the products of reactions of ion radicals is concerned with the competition between reaction channels arising from the presence of an unpaired electron (radical chemistry, electron transfer) and those that are a consequence of the charge (electrophile/nucleophile reactions). While the distinction seems conceptually simple, in practice it is difficult because, after the initial process, further steps are necessary before the final product is reached, and this can lead to complex behavior that leaves considerable latitude for interpretation. The redox reactions of diazo compounds provide additional complexity; the ion radicals of diazo compounds are ambident species with potential reaction centers on the diazo carbon atom and terminal nitrogen atom, and, in these situations in which unimolecular nitrogen loss occurs, further competition arises in the reaction of the carbene ion radical. The possibilities for interpreting observed reaction products are multifarious, and, in the absence of additional evidence, caution is necessary.

These difficulties may be illustrated by considering the products of reduction of Ph₂CN₂ in aprotic solvents containing no added protic compounds.^{10,31,37} The isolated products consist of benzophenone azine (Ph₂C=NN=CPh₂), benzophenone hydrazone (Ph₂C=NNH₂), and diphenylmethane, together with a little Ph₂CO and Ph₂CHNHN=CPh₂. The origin of Ph₂CH₂ could be either Ph₂CN₂^{•-} or the derived Ph₂C^{••-} by one or more of the paths in Scheme II. Additional information is required such as the observation of kinetic solvent deuterium isotope effects on the disappearance of Ph₂CN₂^{•-} in CD₃CN or DCON-(CD₃)₂,³¹ of increased yields of hydrazone and more rapid consumption of Ph₂CN₂^{•-} in the presence of good proton donors ROH, of temperature effects on the ratio of Ph₂CH₂ to Ph₂C=NNH₂, and of the magnitude of *n* values.³⁸ These indicate that, depending on the conditions, both hydrogen atom and proton abstraction by Ph₂CN₂^{•-} occur with no involvement of the carbene

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(38) Cheng, S.; Hawley, M. D. *J. Org. Chem.* 1986, 51, 3799.

anion radical in this instance. The example serves to underline the need for both product and kinetic information under a variety of conditions in order to elucidate fully the complexity of apparently simple chemistry. Direct kinetic study of the behavior of carbene ion radicals in solution has not proved possible and here reliance must be on product identity and proportions under varying conditions in conjunction with n values.

The determination of the number (n) of electrons consumed per molecule of diazo compound that is decomposed can shed light on the reaction channel even when direct kinetic investigation is not feasible. Three limiting situations arise in the electrolysis of diazo compounds.

(i) $n < 1$. Each electron causes the consumption of several molecules of the diazo compound, signifying the operation of a chain reaction normally producing the corresponding azine as in the reduction of 9-diazo-fluorene³⁹ and Ph_2CN_2 .³⁷

(ii) $n = 1$. Since no further electron is involved after the generation of $\text{RR}'\text{CN}_2^{*+/-}$, this signifies that its behavior, or that of derived ion radicals, e.g., carbene ion radicals, is dominated by the unpaired electron, giving atom abstraction with subsequent polar reaction steps, such as proton transfer, to yield the isolated products.

(iii) $n = 2$. The formation of an intermediate capable of readily accepting an electron from or giving up an electron to, usually, $\text{R}_2\text{CN}_2^{*+/-}$ is indicated, and this is associated with the formation of neutral free radicals by reaction of cation radicals with nucleophiles or anion radicals with proton donors. Note that other reactions of the intermediate radical not involving electron transfer, e.g., H abstraction, would give rise to $n = 1$.

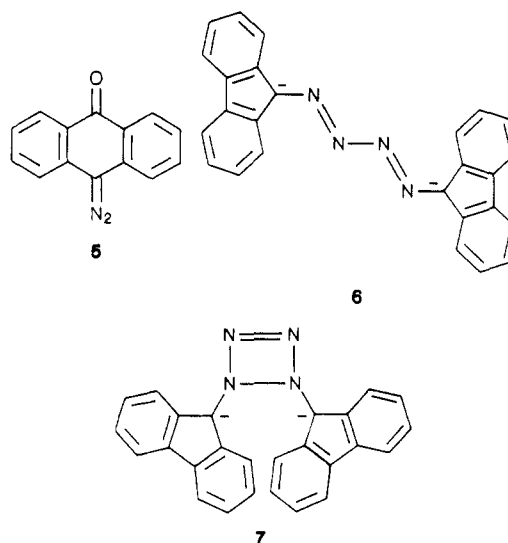
Finally, we draw attention to the observation of apparently conflicting n values for the same reaction under different conditions. The reduction of 9-diazo-fluorene has been shown by voltammetric studies to follow an eC_{dim} mechanism,³⁰ implying the consumption of 1 electron per diazoalkane molecule reacting. If the disappearance of the diazo compound on a preparative scale in a stirred reactor is followed as a function of the number of electrons consumed, n is found to be around 0.02 F mol^{-1} .³⁹ The time scale of the electrode kinetic studies is of the order of milliseconds, whereas that of the preparative experiment is of the order of kiloseconds; clearly different chemical processes are being scrutinized. In the quiet solutions of the former case, $\text{RR}'\text{CN}_2^{*-}$ finds another $\text{RR}'\text{CN}_2^{*-}$ as the most abundant and reactive partner during its short lifetime. In stirred reactions with low current densities $\text{RR}'\text{CN}_2^{*-}$ (or derived intermediates) may encounter molecules of the parent diazo compound, thereby initiating a chain process, the kinetic parameters of which may give rise to apparent rates quite different from those of the initiating steps.

A somewhat similar situation arises in the reduction of azibenzil (ABN_2); the voltammetric results indicate, as we have seen, an eC mechanism, but with n usually between 1 and 2,¹¹ while preparative electrolyses yield apparent n values $\ll 1$.³³ The chain reaction in this case turns out to be a secondary reaction of the electro-

chemical product, the carbanion ABH^- , PhCO(Ph)CH^- with the precursor diazoketone in which electron transfer plays no part.³⁴ This example underlines the importance of ensuring that the products are indeed those arising directly from the intermediates under investigation.

Reaction Channels for Anion Radicals $\text{RR}'\text{CN}_2^{*-}$ and $\text{RR}'\text{C}^{*-}$. The kinetic form of the consumption of $\text{RR}'\text{CN}_2^{*-}$ provides basic information about the pathways followed by the species formed at the electrode. Reaction channels reported include (i) dimerization, (ii) reaction with $\text{RR}'\text{CN}_2$ leading to a chain reaction, (iii) hydrogen atom abstraction from the medium, (iv) protonation in the presence of good proton donors such as $\text{CH}_2(\text{CO}_2\text{Et})_2$ and $\text{CF}_3\text{CH}_2\text{OH}$, and (v) unimolecular N_2 loss.

Anion radical dimerization is dominant in the reduction of 9-diazo-fluorene³⁰ but has also been observed in the case of 10-diazoanthrone (5) at low temperature.⁸



The redox behavior of the products of dimerization has been examined voltammetrically, and, by elegant experiments from Hawley's group in which pressure measurements were made in conjunction with the voltammetry, signals in the cyclic voltammogram could be assigned to the reoxidation of the dimer dianion and dimer anion radical.⁴⁰ Voltammetry at lower temperatures indicated that these dimer signals are accompanied by one indicative of a two-electron reoxidation of an additional species.⁴¹ At intermediate temperatures, this intermediate could be seen to decrease in concentration, disappearing completely above -25°C . On oxidation it gives rise to the dimer mentioned above, together with fluorenone azine. Two dimeric structures are indicated, that which persists to relatively high temperatures on the cyclic voltammetry time scale being assigned the linear structure 6. The structure of the species detectable only below -25°C is problematical, but faute de mieux the cyclic structure 7 has been tentatively suggested for this dimer dianion. Both types of dimer are transformed to fluorenone azine ultimately.

In situations in which the anion radical of 9-diazo-fluorene is generated in the presence of relatively high

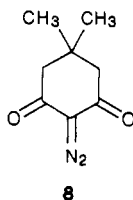
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concentrations of the parent diazo compound, a chain reaction is initiated, with chain lengths of 50 or more, leading to fluorenone azine as the sole product.³⁹ Kinetic analysis of electrolyses at constant current and experiments in which the extent of further consumption of the diazo compound after interruption of the current have shown that the propagation step has the kinetic form $v_p = k_p[C][FIN_2]$, where $[C]$ is the concentration of the chain carrier generated at the electrode. It has been argued that the magnitude of k_p , ca. $10 \text{ M}^{-1} \text{ s}^{-1}$ at 30°C , is consistent with an endoergonic electron-transfer process from C to the diazocompound. The anion radical of fluorenone azine is the obvious candidate for C ; the anion radical of the more persistent dimer of 9-diazofluorene could also be involved, but ^{15}N -labeling studies, in which monolabeled FIN_2 gave largely monolabeled product azine, suggest only a minor role for this intermediate.⁴¹ A more complex combination of intermediates has been suggested for the corresponding chain reaction of Ph_2CN_2 .³⁸

Proton transfer to $\text{RR}'\text{CN}_2^{\bullet-}$ seems to occur in all but those cases where rapid dimerization takes place. The anion radical is ambident but protonation on carbon leading, after N_2 loss and a second electron transfer, to the corresponding carbanion is the more important pathway (Scheme II), at least with the less acidic proton sources.³⁷ Benzoic acid, however, leads to high yields of hydrazone from $\text{Ph}_2\text{CN}_2^{\bullet-}$, and this product is favored with weaker acids when the reaction temperature is lowered. The apparent preference for C-protonation has been attributed³⁸ to basicity differences between C and N, although the irreversibility of N_2 loss after C-protonation, contrasting with the competition after N-protonation between electron transfer and deprotonation, may influence the chemical outcome. Other $\text{RR}'\text{CN}_2^{\bullet-}$ undergo protonation but the pattern of behavior is not yet properly understood. Thus $\text{PhCO}(\text{Ph})\text{CN}_2^{\bullet-}$ is rapidly protonated by phenol ($\text{p}K_a^{\text{DMSO}} = 13$),¹¹ $(\text{EtO}_2\text{C})_2\text{CN}_2^{\bullet-}$ is not protonated even by PhCO_2H ($\text{p}K_a^{\text{DMSO}} = 11$),⁴² while the anion radical of diazodimedone (8) is protonated rapidly by $\text{CF}_3\text{CH}_2\text{OH}$ ($\text{p}K_a^{\text{DMSO}} = 23$) but not by $(\text{EtO}_2\text{C})_2\text{CH}_2$ ($\text{p}K_a^{\text{DMSO}} = 16.4$).⁴³ Further investigation of the relationship between charge distribution in $\text{RR}'\text{CN}_2^{\bullet-}$ and protonation is clearly necessary.



Four examples are now known of unimolecular fragmentation of $\text{RR}'\text{CN}_2^{\bullet-}$ to give $\text{RR}'\text{C}^{\bullet-}$. Three of these are α -diazocarbonyl compounds, and in each case the final product is the corresponding carbanion. In the fourth case, tetraphenyldiazocyclopentadiene³⁴ (cf. Webster's early observation on the tetracyanocompound²⁵), no carbonyl group is present but the $\text{RR}'\text{C}$ moiety has a similar ability to accommodate a negative charge as judged by the values of $\text{p}K_a^{\text{DMSO}}$ of

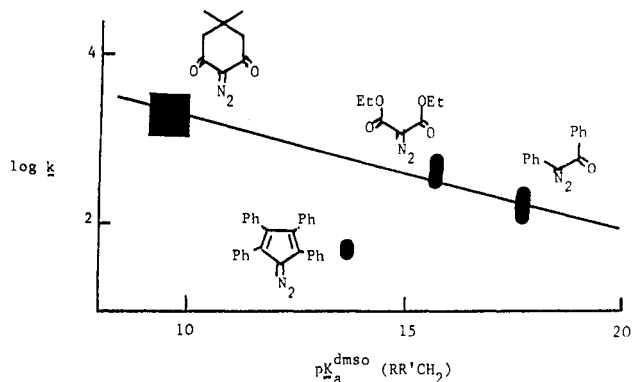


Figure 1. $\log k$ vs $\text{p}K_a^{\text{DMSO}}(\text{RR}'\text{CH}_2)$.

$\text{RR}'\text{CH}_2$. Figure 1 (constructed with generous allowance for uncertainties in the first-order rate coefficient k for N_2 loss arising from differences in solvent and from the mixed eC/eC_e character of the reactions) shows that there is a rough parallelism between the rate of loss of N_2 and the ability of carbonyl-containing groups $\text{RR}'\text{C}$ to distribute the charge, but the slope is only ca. 0.2, and this suggests a relatively small increase in the need for charge stabilization on passing from $\text{RR}'\text{CN}_2^{\bullet-}$ to the transition state. The observation that, in the group, the one diazo compound with no α -carbonyl falls well below the line underscores the need for data from a wider range of diazo compounds. It is tempting to suggest, however, that it is a manifestation of the varying need, recently emphasized in a different context by Bordwell,⁴⁴ for negative charge and odd-electron stabilization in $\text{RR}'\text{CN}_2^{\bullet-}$ and $\text{RR}'\text{C}^{\bullet-}$. Nevertheless it is not surprising that unimolecular N_2 loss is not observed for 9-diazofluorene or Ph_2CN_2 in view of the much higher values of $\text{p}K_a^{\text{DMSO}}$ for the corresponding hydrocarbons.

The dominant reaction of $\text{RR}'\text{C}^{\bullet-}$, in those cases where the formation of such intermediates has been detected kinetically, is transformation into the corresponding carbanion $\text{RR}'\text{CH}^-$. Possible routes are by H-atom abstraction ($n = 1$) or by protonation followed by electron transfer ($n = 2$). Depending on the conditions, particularly the solvent, these pathways compete ($1 < n < 2$); for example $(\text{EtO}_2\text{C})_2\text{C}^{\bullet-}$ gives $n = 1$ in DMF solution but ca. 1.5 in the poorer H^+ -donating solvent CH_3CN (but see ref 9).¹¹ In view of this and the observed effects of proton donors on the behavior of $\text{RR}'\text{CN}_2^{\bullet-}$, Webster's suggestion that tetracyanocyclopentadienylidene anion radical is capable of direct nuclear substitution in phenol needs to be reconsidered.

Reaction Channels for Cation Radicals $\text{RR}'\text{CN}_2^{\bullet+}$ and $\text{RR}'\text{C}^{\bullet+}$. The kinetic studies have shown that single-electron oxidation of diazo compounds can be followed by (i) dimerization of $\text{RR}'\text{CN}_2^{\bullet+}$ as in the case of 9-diazofluorene and certain monoaryl diazoalkanes, $\text{Ph}(\text{R})\text{CN}_2$, (ii) reaction with nucleophiles, both anionic and neutral, and (iii) unimolecular N_2 loss, giving carbene cation radicals.

The reaction with nucleophiles is the most general one, anionic nucleophiles being much more reactive than neutrals such as pyridines or methanol. Hydroxylic nucleophiles give rise to proton generation in reaction mixtures, and these can give rise to acid-cata-

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(43) Van Galen, D. A.; Hawley, M. D. *J. Electroanal. Chem.* 1987, 218, 227.

(44) See, for example: Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* 1986, 108, 1979. Bordwell, F. G.; Wipson, C. A. *Ibid.* 1987, 109, 5470.

lyzed reactions that complicate the interpretation of reaction products.³⁶ Low concentrations of sterically hindered pyridine bases usually suppress acid catalysis. In all cases so far examined, oxidation of diazo compounds in the presence of nucleophiles leads to more rapid consumption of $RR'CN_2^{*+}$ than in the absence of nucleophiles in a process for which $n = 2$.⁸ This indicates that the adduct of $RR'CN_2^{*+}$ + nucleophile undergoes a further oxidation either before or more probably after nitrogen loss in those cases where nucleophilic attack is at the diazocarbon atom. The formation of benzophenone from the oxidation of Ph_2CN_2 in the presence of excess acetate ion is consistent with this.

Perhaps for steric reasons, as well as the ability to delocalize the positive hole, the cation radicals of Ph_2CN_2 , **3**, and **4** show low reactivity toward low concentrations of electrically neutral nucleophiles, and this has permitted unimolecular loss of N_2 to be observed.³⁵ Although the $RR'C$ moieties span a wide range of abilities to accommodate positive charge as judged by pK_{R^+} values for $RR'CH^+$ (-3 to -13), there is no obvious relation to the rate of N_2 loss. $Ph_2CN_2^{*+}$ shows a rate of N_2 loss intermediate between that of **3** (slower) and that of **4** (faster) despite the Ph_2C grouping having the poorest charge-stabilizing ability. The resultant carbene cation radicals, when generated in methanol solution, rapidly react to give product mixtures that consist largely of $RR'CHOMe$, $RR'(OMe)_2$, and $RR'C=O$. The observed n value is close to unity when the percentage yield of the first of these products is high and approaches 2 as the yield drops toward 0%. The implication is that $RR'CHOMe$ is formed by H-atom abstraction from the solvent methyl group, leading to $RR'CH^+$ followed by nucleophilic attack by the solvent. $RR'C=O$ and $RR'(OMe)_2$ result from nucleophilic attack by solvent on the carbene cation radical, giving $RR'COMe$ after loss of H^+ , followed by a favorable one-electron oxidation to $RR'C^+OMe$ and capture by the solvent. Consistent with this interpretation, the carbene cation radical from **4**, which has the greatest facility to delocalize positive charge, gives the highest yield of ether product in preparative electrolyses. Interestingly, in view of the failure of correlations of the rate of N_2 loss (k) with pK_{R^+} for $RR'CH^+$, there appears to be a rough parallelism between k and the observed product ratio $[RR'CHOMe]/([RR'C=O] + [RR'(OMe)_2])$ or the ratio R of one-electron:two-electron pathways as given by $R = (n - 1)/(2 - n)$. Again, a more extensive range of diazo compounds needs to be studied before the generality of this correlation will be established and need interpretation.

The very rapid dimerization of electrochemically generated diazoalkane cation radicals has been demonstrated kinetically for 9-diazo fluorene⁴⁵ and inferred in chemical oxidations on the basis of product structure and reaction stoichiometry in the case of 1-phenyl-2-mesityldiazoethane.⁴⁶ In general, the products are mixtures of symmetrical azines together with dimeric olefins (dehydro dimers). Although experiments were carried out in rigorously dry solvents, product studies were not carried out in the presence of nonnucleophilic

Table III
Activation Parameters for N_2 Loss and Estimated Thermodynamics of Electron Transfer between Diazo Compounds and Carbene Ion Radicals

reaction	ref	ΔH^\ddagger / kcal mol ⁻¹	ΔS^\ddagger / cal K ⁻¹ mol ⁻¹
$Ph_2CN_2 \rightarrow Ph_2C: + N_2^a$	48	27.2	0
$Ph_2CN_2^{*+} \rightarrow Ph_2C^{*+} + N_2^a$	35	15.5	-3.5
$Ph_2C^{*+} + Ph_2CN_2 \rightarrow Ph_2C: + Ph_2CN_2^{*+}$		11.7	3.5
$(EtO_2C)_2CN_2 \rightarrow (EtO_2C)_2C: + N_2^b$	49	30	8
$(EtO_2C)_2CN_2^{*-} \rightarrow (EtO_2C)_2C:^{-} + N_2^a$	11	10.6	-7
$(EtO_2C)_2C:^{-} + (EtO_2C)_2CN_2 \rightarrow (EtO_2C)_2C: + (EtO_2C)_2CN_2^{*-}$		19.4	15
$PhCO(Ph)CN_2 \rightarrow PhCO(Ph)C: + N_2^b$	49	35	14
$PhCO(Ph)CN_2^{*-} \rightarrow PhCO(Ph)C:^{-} + N_2^a$	11	12.7	-0.7
$PhCO(Ph)C:^{-} + PhCO(Ph)CN_2 \rightarrow PhCO(Ph)C: + PhCO(Ph)CN_2^{*-}$		22.3	14.7

^a Solvent CH_3CN . ^b Solvent mesitylene.

bases, and this leaves open the possibility that acid-catalyzed pathways could give rise to some products. Initial reaction of $RR'CN_2^{*+}$ or derived species such as the dimeric dication with protic nucleophiles, e.g., H_2O , could generate protons. Electrochemical initiation of the proton-catalyzed decomposition of Ph_2CN_2 has been described. Nevertheless there is prima facie evidence for reactions of $RR'CN_2^{*+}$ with the parent diazo compound to give azine in competition with dimerization.^{46,47}

Electron Transfer. Finally, we address the problem of electron-transfer reactions of carbene ion radicals. Under the conditions of the experiments in which carbene ion radicals have been shown to be generated, the obvious species to participate in electron transfer by receiving an electron from $RR'C:^{-}$ or donating one to $RR'C^{*+}$ is the precursor diazo compound; this would lead to a chain reaction. From known activation parameters for thermal N_2 loss from the parent compound and from derived ion radicals, it can be seen that such a reaction pathway is likely to be unfavorable. Combination of the appropriate figures, ignoring solvent effects and assuming that transition states for the formation of $RR'C:$ and the related ion radicals approximate to the intermediates themselves, yields the results in Table III for $Ph_2C:/Ph_2C^{*+}$, $(EtO_2C)_2C:/ (EtO_2C)_2C:^{-}$, and $PhCO(Ph)C:/PhCO(Ph)C:^{-}$. The highly endothermic nature of the electron-transfer process makes it highly improbable that it will be able to compete with the other reaction channels of carbene ion radicals discussed earlier.

Current Status and Prospects

The behavior of ion radicals of diazo compounds is a lively area of study. The generation of carbene anion and cation radicals has been demonstrated. Their formation appears to be much easier and more widespread than thought hitherto, and their patterns of chemical behavior are beginning to emerge. Indeed, a recent report⁵⁰ has claimed the direct observation by

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ESR spectroscopy of $RR'CN_2^{*+}$ and, after photolysis, the derived carbene cation radical, although the absence of resolved hyperfine coupling means that the assignment of structure is largely circumstantial.

Synthetic application of this chemistry seems unlikely at present because of the multiplicity of reaction channels available both to $RR'CN_2^{*+/-}$ and to $RR'C^{*+/-}$. However, as further information on a wider spectrum of structures of diazo compounds becomes available, this preliminary assessment may have to undergo re-

vision. Indeed, this chemistry will need to be borne in mind if recent interest in the cycloaddition of alkene cation radicals to diazo compounds⁵¹ is to be extended.

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Direct Electrochemistry of Redox Proteins

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Among studies of electron-transfer reactions of proteins, the area of direct (i.e., unmediated) electrochemistry has interested us for several reasons: First, from an innovatory viewpoint, a marriage between electrode materials and biological macromolecules that bear highly specific modes of catalytic or sensory action is highly desirable. Second, as with electrochemical reactions of simpler molecules, we are able to obtain important information about intrinsic thermodynamic and kinetic properties. Third, since direct electrochemistry is observed only after the problems of interfacial specificity, compatibility, and denaturation have been overcome, we stand to learn much about the dynamic operation of macromolecular interfaces, and this has far-reaching implications. Studies undertaken in this laboratory, as well as in several others, have sought to explore this "new" field and to define the relationships between electrochemistry, colloid and interface science, and biochemistry. A "thought tree" illustrating our view of the connectivities in this area is shown in Figure 1.

The simplest redox proteins are those whose only established role is to convey electrons. They are comparatively small, with molecular masses in the range

5-20 kDa, and, as a class, have been characterized extensively with regard to structure and function. It may be said that the cytochromes, the "blue" copper proteins, and the iron-sulfur proteins are today as familiar to chemists as they are to biochemists. Thus the idea of an electron-transfer protein displaying reversible or quasi-reversible cyclic voltammetry analogous to that of a small redox reagent such as ferrocene may seem straightforward. Yet it embraces a contradiction: from various studies of electron-transfer reactions between protein molecules, the emerging consensus emphasizes the requirement for fast and reversible formation of an intimate, precursory, donor-acceptor complex docked so as to maximize the rate of electron transfer between redox centers. By contrast, in outer-sphere electron transfer between small inorganic molecules precursor complex formation is generally undetectable and of much less mechanistic significance.

If we consider the electron-transfer reactivity of a protein at an *electrode*, then the requirement for intimate precursory interaction merges uncomfortably with the well-known tendency of proteins to undergo irreversible adsorption coupled with conformational changes and loss of activity. Electrode "fouling" by biological material is indeed a familiar problem in bioelectrochemistry, yet the now-routine measurements of protein voltammetry, with standards of reversibility comparable to those seen with the redox couples of small molecules, demonstrate clearly that this can be avoided under appropriate conditions. We believe that this reflects provision, at the electrode interface, of the essential elements of macromolecular recognition, i.e., complementary hydrogen bonding, salt bridging, and hydrophobic contacts, that are important in a protein's interactions with its physiological partners. Our own approach has been to evaluate systematically the interactive characteristics of electron-transfer proteins and thenceforth venture upward in complexity toward the achievement of clear and well-defined electrochemistry of larger enzymes. In this Account we discuss some of the more salient findings and their implications.

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