Carbene Cation Radicals: The Kinetics of Their Formation from Diazoalkane Cation Radicals and Their Reactions

Vernon D. Parker*[†] **and Donald Bethell***[‡]

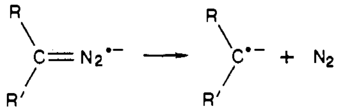
Contribution from the Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway, and the Department of Organic Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England.

Received February 11, 1987

Abstract: The unimolecular decomposition reactions of three diazoalkane (diazodiphenylmethane and related compounds) cation radicals were studied in acetonitrile, methanol, and mixed solvent. Kinetic studies, using transient electrochemical methods, show that the reaction rates are insensitive to solvent, the presence of nucleophiles, and the nature and concentration of electrolytes. At temperatures above 300 K the competing second-order reactions, observed to minor extents at lower temperatures, were insignificant. Arrhenius activation energies were observed to be of the order of 16 kcal/mol with entropies of activation close to zero. It is suggested that the rate-determining step in all cases is unimolecular loss of dinitrogen (reaction i) to generate the reactive carbene cation radicals. The carbene cation radicals show reaction patterns that exhibit both electrophilic and radical-like facets. In acetonitrile complex reaction mixtures were obtained suggesting that the carbene cation radicals react rather indiscriminately. In more nucleophilic methanol, the major products were $Ar_2C(OMe)_2$, $Ar_2C{=}O$, and Ar_2CHOMe in proportions depending strongly on the structure of the carbene cation radical.

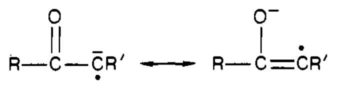
$$Ar_2C{=}N_2^{\bullet +} \rightarrow Ar_2C^{\bullet +} + N_2 \qquad \text{(i)}$$

Recent work has demonstrated that carbene anion radicals can be generated in solution from the corresponding anion radicals of diazo compounds of appropriate structure.[1-4] The characteristic features of the unimolecular decomposition reaction 1 are that they have relatively high activation energies and only take place



$$RR'C{=}N_2^{\bullet -} \longrightarrow RR'C^{\bullet -} + N_2 \qquad (1)$$

when there is extensive delocalization of the negative charge.[3] The first carbene anion radicals generated in solution have carbonyl groups adjacent to the carbene center[1-3] and can be represented by the canonical forms, **1** and **2**, the latter having the features of a vinyl radical.



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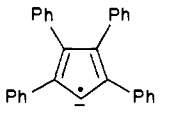
The generation of a hydrocarbon analogue (**3**) demonstrated that the adjacent carbonyl is not a prerequisite for carbene anion radical formation as long as charge delocalization can accommodate the negative charge.[4] It was found that the ease of formation of carbene anion radicals in solution is related to the pK_a values of the corresponding carbon acids, **4**.

The failure to observe reactions 1 with diazodiphenylmethane[5,6] and 9-diazofluorene[7-9] anion radicals can be accounted for on the basis of the carbon acid pK_a carbene anion radical formation relationship[4] along with the fact that facile alternative reaction pathways exist. Both of these anion radicals were, before kinetic data became available, believed to undergo reaction 1 in aprotic solvents.[10,11]



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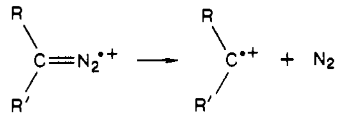
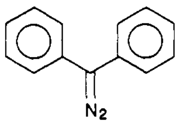
$R—CH_2—R'$

4

In this paper we report the first kinetic demonstrations of the formation of carbene cation radicals in solution. The carbene cation radicals may be generated by unimolecular cleavage of dinitrogen from the corresponding diazoalkane cation radicals in acetonitrile or methanol solutions (reaction 2). The substrates (**7**, **8**, **9**) form cation radicals that are relatively long-lived at ambient temperature in both aprotic and hydroxylic solvents and show unusually low reactivity toward nucleophiles such as methanol and pyridine. These substrates were chosen in view of our experience with carbene anion radicals which suggested that the ability of the hydrocarbon moiety to stabilize a positive charge should be a deciding factor in the successful generation of carbene cation radicals. Again, as in the case of reaction 1, unimolecular decomposition reactions 2 are observed to have high activation energies as their distinguishing feature.



$$RR'C{=}N_2^{\bullet +} \longrightarrow RR'C^{\bullet +} + N_2 \qquad (2)$$



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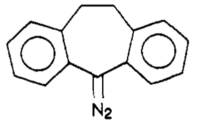

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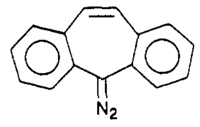

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Diazoalkane cation radicals are obvious potential sources of carbene radicals by unimolecular loss of dinitrogen.

Early studies in this area have been reviewed by Fry,[12] but in general unambiguous experimental evidence has been lacking. For example, the simplest carbene cation radical $CH_2^{\bullet +}$ was suggested

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[‡] University of Liverpool.

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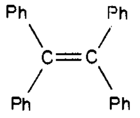
Table I. Oxidation Peak Potentials and Cation Radical Lifetimes in Acetonitrile[a]

substrate	E^p (V) vs. Ag/Ag$^+$	half-life[b] (s)
7	+0.839	0.11
8	+0.760	0.08
9	+0.661	0.017

[a] In solutions containing Et_4NBF_4 (0.1 M) and substrate (1.0 mM) at 289 K. [b] Estimated by DCV assuming the eCe$_h$ mechanism.

to be formed by electrochemical oxidation of diazomethane in sulfolane largely on the basis of the formation of methylpyridinium ion when pyridine was present.[13] More recently we have shown that the cation radical of 9-diazofluorene generated in acetonitrile at a platinum anode is consumed in a very fast second-order process, presumed to be dimerization.[14] Carbene cation radical formation was not to be expected in this case since the fluorenylidene structure is inappropriate for the delocalization of positive charge. Rather more surprising was the observation of Little and Schuster[15] that electrooxidation of phenylmesityldiazoethane, $PhC(N_2)CH_2Mes$, yields a mixture of dehydro dimers ($C_{34}H_{34}$) and the symmetrical azine, suggesting that the cation radical of the diazo compound undergoes dimerization in competition with attack on the parent molecule. Previous studies[16,17] on the oxidation of **7** in acetonitrile either electrochemically or with chemical oxidants showed that upon generating catalytic amounts of $\mathbf{7}^{\bullet+}$ a chain decomposition of **7** occurs leading to tetraphenylethylene (**10**) and the azine **11** as the major products. A more recent study has conclusively shown that $\mathbf{7}^{\bullet+}$ is not the chain carrier but rather that the reaction is catalyzed by protons generated upon interaction of $\mathbf{7}^{\bullet+}$ with nucleophiles.[18] Thus, after electrochemical initiation, the chain reaction does not take place in the presence of low concentrations of the base, 2,6-lutidine, which does not react with the cation radical.



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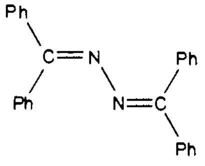

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Results

Ease of Formation and Stability of Cation Radicals of Diazoalkanes. The results of a preliminary derivative cyclic voltammetry (DCV) study of the generation of cation radicals from **7**, **8**, and **9** are summarized in Table I. The peak potentials were measured at a voltage sweep rate (ν) of 100 V s^{-1}, conditions under which further reactions of the cation radicals do not affect the measurements. These show that as the molecule becomes more planar, the reversible potential becomes less positive, reflecting a smaller change in structure between the neutral substrate and the cation radical. All three substrates are easily oxidized and the cation radicals are relatively long-lived, allowing observation by slow sweep cyclic voltammetry. The latter is reflected in the half-lives determined by DCV assuming an eCe$_h$ mechanism (electrode reaction followed by rate-determining chemical reaction and fast homogeneous electron transfer).

Qualitative results of the effect of nucleophilic additives, water, methanol, and 2,6-lutidine indicated that nucleophiles do not increase the rate of decomposition of the cation radicals. Furthermore, addition of neutral alumina to the solution,[19] in order to remove protic and nucleophilic impurities, had no observable effect on the results of the DCV experiments.

Table II. Effect of Solvent on the Rate of Decomposition of Diazoalkane Cation Radicals[a]

CH_3CN/ CH_3OH	$\nu_{1/2}$[b] (V·s^{-1})		
	7	**8**	**9**
5/0	6.57	4.22	22.0
2/1	8.83	3.76	26.1
1/2	5.27	2.46	25.9
0/5	4.72	2.50	21.0

[a] In solvent containing Et_4NBF_4 (0.1 M) and substrate (1.0 mM) at 313.2 K. [b] The voltage sweep rate necessary for the derivative peak ratio R_I' to equal 0.500 with $E_{sw} - E_{rev}$ = 200 mV.

Table III. The Effect of Pyridine on the Rate of Decomposition of Diazoalkane Cation Radicals in Methanol at 313.2 K[a]

[pyridine]/ mM	$\nu_{1/2}$[b] (V·s^{-1})		
	7	**8**	**9**
0	7.37	6.08	17.5
10	6.87	3.24	17.4
20	6.85	3.39	17.5
40	7.96	3.59	18.9

[a] In solvent containing $NaClO_4$ (0.1 M) and substrate (1.0 mM). [b] As defined in Table II.

Table IV. The Effect of Substrate Concentration on the Rate of Decomposition of Diazoalkane Cation Radicals in Methanol[a]

C_A (mM)	$\nu_{1/2}$[b] (V·s^{-1})		
	7	**8**	**9**
0.50	25.7	20.5	80.8
1.00	31.1	20.0	86.3
2.00	39.7	23.4	88.9
4.00	48.4	21.9	93.1

[a] In solvent containing $NaClO_4$ (0.1 M) and pyridine (10 mM) at 333.2 K. [b] As defined in Table II.

Solvent Effect on Apparent Rate Constants. The voltage sweep rate necessary to observe a derivative peak ratio equal to 0.500, $\nu_{1/2}$, is a convenient measure of the apparent rate constants of electrode reactions.[20] Use of this quantity does not require a knowledge of the detailed mechanism, and the specific rate constants can be obtained directly from $\nu_{1/2}$ once the mechanism has been established.

The effect of changing the solvent composition from pure acetonitrile to pure methanol on $\nu_{1/2}$ is illustrated by the data in Table II. With substrates **7** and **9** addition of methanol to acetonitrile solutions brought about first an increase in $\nu_{1/2}$ and then a decrease so that the value in pure methanol was lower than that in acetonitrile. With substrate **8** the maximum in $\nu_{1/2}$ with increasing [MeOH] was not observed. These results indicate that the solvent effect is small and dependent upon the particular cation radical undergoing decomposition.

The Effect of Pyridine on Apparent Rate Constants. The very low susceptibility of the cation radicals to nucleophilic attack is shown by the data in Table III. None of the cation radicals showed increased reactivity in the presence of pyridine at concentrations as high as 40 mM. The addition of pyridine to solutions containing **8** resulted in appreciably lower values of $\nu_{1/2}$ for the reaction of the cation radical.

These results are of especial practical importance for the study of these reactions, since all the substrates undergo acid-catalyzed chain decompositions and the origin of products of preparative experiments becomes uncertain, unless it is possible to control the proton activity by the presence of a suitable base.

Reaction Order Studies of Cation Radical Decomposition. The reaction order in cation radical can be derived from the effect of

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Table V. Electrolyte and Deuteriated Solvent Effect on the Rate of Decomposition of $9^{\cdot+}$ in Methanol[a]

	$\nu_{1/2}$[b] ($V \cdot s^{-1}$)		
C_A/mM	CH_3OH/Et_4NBF_4 (0.1 M)	$CH_3OH/NaClO_4$ (0.1 M)	$CD_3OD/NaClO_4$ (0.1 M)
0.50	20.9	16.9	17.0
1.00	24.4	19.0	18.0
2.00	22.5	18.6	18.3
	22.6 ± 1.8	18.2 ± 1.1	17.8 ± 0.5

[a] At 313.2 K. [b] As defined in Table II.

Table VI. Electrolyte Effect on the Rate and Activation Parameters for the Decomposition of $9^{\cdot+}$ in Acetonitrile

electrolyte	$\nu_{1/2}$[a] ($V \cdot s^{-1}$)	E_a[b] (kcal/mol)	r[c]
Me_4NBF_4 (0.05 M)	1.46	16.4	0.998
Et_4NBF_4 (0.1 M)	1.47	16.2	1.000
$LiClO_4$ (0.1 M)	1.42	16.7	1.000
$LiClO_4$ (0.1 M) (CD_3CN)	1.42	16.7	1.000

[a] For measurements at 273.2 K, as defined in Table II with $E_{sw} - E_{rev}$ = 300 mV. Substrate concentration, 1.0 mM. [b] For measurements at 0, 15, 30, and 50 °C. [c] Correlation coefficient of the Arrhenius plot.

substrate concentration on $\nu_{1/2}$ according to eq 3.[20] In (3) $R_{A/B}$ is the composite reaction order in substrate A and, in this case,

$$R_{A/B} = 1 + d \log \nu_{1/2}/d \log C_A \qquad (3)$$

cation radical B and the second term on the right is the slope of a log–log plot of $\nu_{1/2}$ vs. substrate concentration. A slope of zero gives $R_{A/B}$ equal to unity, indicating that the reaction order in cation radical is equal to 1.

The data in Table IV illustrate the effect of substrate concentration on $\nu_{1/2}$ for the three substrates at 333.2 K in methanol containing Et_4NBF_4 (0.1 M). For substrates **8** and **9** the slopes of log $\nu_{1/2}$ vs. log C_A plots are zero or very nearly so, indicating reactions first order in cation radical. With substrate **7**, $\nu_{1/2}$ very nearly doubled as C_A was increased eightfold. This gives rise to a log–log plot slope of 0.3 and an apparent reaction order of about 1.3. The latter suggests a predominant first-order decomposition with a minor second-order component.

Search for Electrolyte and Solvent Involvement in the Cation Radical Decomposition Reactions. We have previously observed that the decomposition reactions of $7^{\cdot-}$ are first-order reactions, which on the surface appear to be compatible with unimolecular decomposition to the carbene anion radical.[5,6] However, large solvent deuterium kinetic isotope effects were observed, implicating hydrogen atom abstraction in the rate-determining steps.

The above observation shows the necessity to check for solvent and electrolyte involvement in the reactions of the cation radicals. The data in Table II argue strongly against the involvement of solvent in the reactions. This, along with the absence of a significant electrolyte effect, is shown by the data in Table V. The average value of $\nu_{1/2}$ in CD_3OD is slightly less than that in CH_3OH, but the deviation is far too small to take as an indication of a primary kinetic isotope effect.

The data in Table VI lead to a similar conclusion for reactions in acetonitrile. Both rate constants and activation energies for the decomposition of $9^{\cdot+}$ in acetonitrile were observed to be essentially independent of the electrolyte and the isotopic content of the solvent.

Effect of Temperature on the Rates of Cation Radical Reactions. Arrhenius plots for the reactions in acetonitrile/Et_4NBF_4 (0.1M) in the temperature range 273.2–326.5 K are shown in Figure 1. Substrate concentrations were 0.5 mM to minimize any interference from second-order reactions, and rate constants were evaluated from $\nu_{1/2}$ assuming the eCe_h mechanism. The slopes correspond to E_a equal to 15.5, 16.6, and 16.2 kcal/mol for $7^{\cdot+}$, $8^{\cdot+}$, and $9^{\cdot+}$, respectively. Plots of log ($\nu_{1/2}/T$) vs. $1/T$, which may be considered to be an Arrhenius relationship,[21] for DCV experiments on 4.0 mM solutions of **8** and **9** in CH_3OH are shown

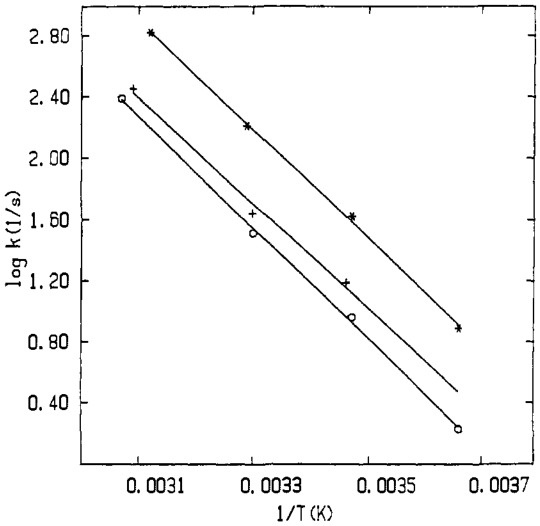

Figure 1. Arrhenius plots for the reaction of diazoalkane cation radicals in CH_3CN solutions containing Et_4NBF_4 (0.1 M). Substrate concentration 0.5 mM: (+) **7**; (○) **8**; (*) **9**. Rate constants were evaluated from $\nu_{1/2}$ assuming an eCe_h mechanism.

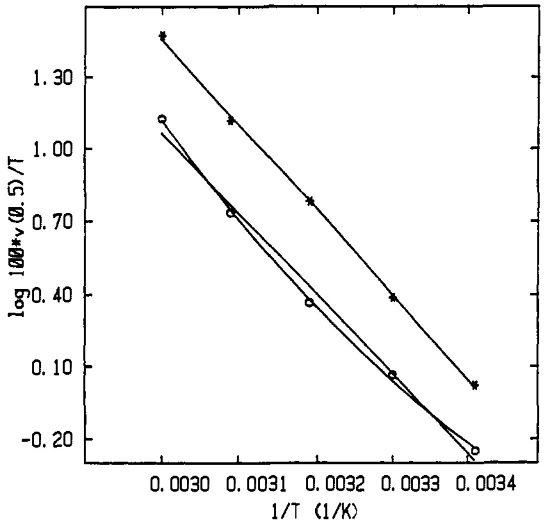

Figure 2. Plots of log ($\nu_{1/2}/T$) vs. $1/T$ from DCV experiments on **8** and **9** in CH_3OH solutions containing Et_4NBF_4 (0.1 M). Substrate concentration 4.0 mM: (○) **8**; (*) **9**.

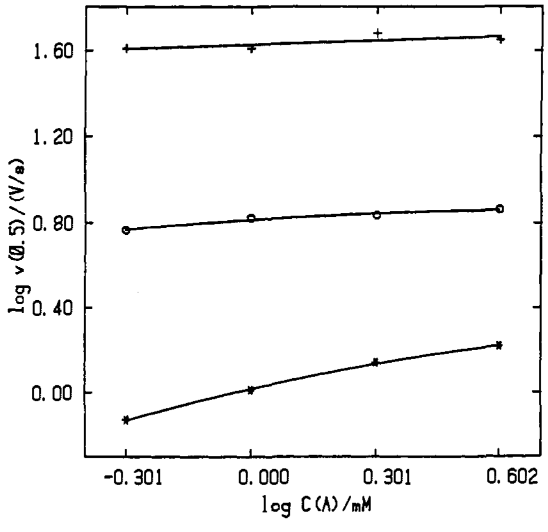

Figure 3. Plots of log ($\nu_{1/2}$) vs. log (substrate concentration) for compound **8** at 293.2 K (*), 313.2 K (○), and 333.2 K (+) in CH_3OH solutions containing Et_4NBF_4 (0.1 M).

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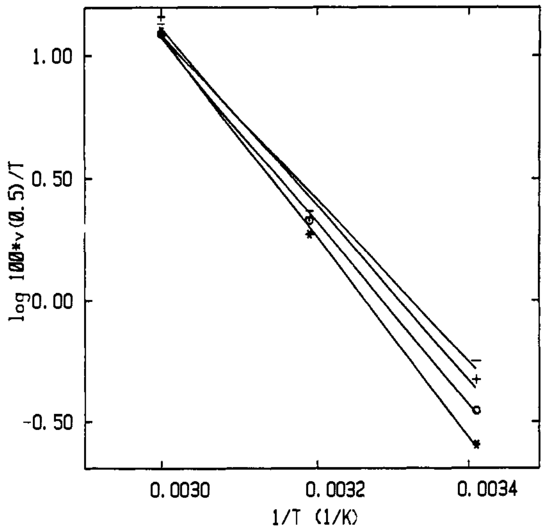

Figure 4. Effect of substrate concentration on Arrhenius-type plots for the reaction of $8^{\bullet+}$ in CH_3OH solutions containing Et_4NBF_4 (0.1 M). Substrate concentrations (mM): 0.5 (*), 1.0 (O), 2.0 (+), and 4.0 (-).

in Figure 2. The curvature for substrate **8**, which is not observed for 0.5 mM solutions, most probably reflects the contribution of second-order reactions at the lower temperatures.

The second-order contribution for reactions of $8^{\bullet+}$ at the lower temperatures is illustrated by the effect of temperature on the reaction order plots shown in Figure 3. At the highest temperature, 333.2 K, first-order behavior is observed with increasing contribution of a second-order pathway as the temperature is lowered first to 313.2 K and then to 293,2 K. Arrhenius plots of these data are shown in Figure 4. Acceptable linearity is only observed for the data obtained at [**8**] equal to 0.5 mM.

The conclusions from these and related experiments is that reactions of $7^{\bullet+}$ and $8^{\bullet+}$ are complicated to a minor degree by second-order pathways at the lower temperatures but not to an appreciable degree at 333.2 K. The decomposition of $9^{\bullet+}$ appears to be first order in cation radical under all conditions investigated.

Rate Constants for the Cation Radical Reactions. Reactions of electrode-generated intermediates are seldom ideal and so a perfect fit of experimental to theoretical data is not to be expected.[20] To circumvent this problem the reaction order approach quantity ($\nu_{1/2}$ for DCV) can be used to derive the rate law for the process without the need to consider a theoretical model. This is essentially what has been done up to now in this paper, and, with the exceptions noted above for lower temperatures, the reactions conform to the rate law in eq 4 where k_{app} indicates an apparent rate constant. In order to relate k_{app} to a specific rate

$$-\mathrm{d}[\text{cation radical}]/\mathrm{d}t = k_{app}[\text{cation radical}] \qquad (4)$$

constant, theoretical data must be used to convert the apparent rate constants ($\nu_{1/2}$ in this work). Rate law 4 is consistent not only with the eCe_h mechanism but also with the eC case (irreversible first-order chemical reaction in an overall one-electron process). Although the eC mechanism is unusual for ion radical reactions, which are usually two-electron processes, carbene ion radicals may undergo atom transfer as well as nucleophilic (or electrophilic) reactions resulting in eC, eCe_h, or mixed behavior. Mixed behavior was observed for carbene anion radicals in previous work.[3]

The electrode responses for the eC and eCe_h mechanisms differ by the number of electrons consumed. The eC mechanism involves one electron irrespective of the degree of conversion while the eCe_h mechanism involves the consumption of two electrons for the complete reaction case and one electron for no reaction. Experimentally, the number of electrons consumed can be determined under conditions used for product studies or, more appropriately for mechanism investigations, under the conditions of the kinetic analysis.

The data in Table VII were obtained by double potential step chronoamperometry (DPSC) oxidations of the substrates in CH_3CN/Et_4NBF_4 (0.1 M) at 313.2 K. The columns labeled I_N are the currents at the end of the forward step normalized to that at $R_I = 0.500$ (R_I is defined as I_f/I_b (0.2929) where I_f and I_b are the currents at τ and 2τ, respectively). For the eC mechanism I_N is invariant at 1.000 while I_N varies from 0.922 ($R_I = 0.750$) to 1.149 ($R_I = 0.200$) for the eCe_h mechanism.[22] The data show that in all cases the experimental values of I_N are very close to the theoretical values for the eCe_h mechanism at R_I between 0.500 and 0.200. At lower conversions the fit is reasonably good for **8** less so for **7**, and the data for **9** fit more closely to the eC mechanism. Coulometric *n* values observed during the preparative experiments indicate that under these conditions two electrons are involved in the oxidation of **8** while between one and two electrons are transferred during exhaustive oxidation of **7** and **9**.

Table VII. DPSC Kinetic Data for the Oxidation of Diazoalkanes in Acetonitrile[a]

	7		8		9	
R_I	k (s^{-1})	I_N	k (s^{-1})	I_N	k (s^{-1})	I_N
0.75	55.6	0.976	31.7	0.951	63.8	0.997
0.70	55.5	0.982	32.0	0.954	72.1	0.997
0.65	55.0	0.991	32.0	0.961	75.3	0.995
0.60	51.8	0.992	31.6	0.970	79.3	0.998
0.55	48.4	0.993	31.0	0.978	80.8	0.999
0.50	46.3	1.000	29.0	1.000	80.2	1.000
0.45	46.4	1.015	28.3	1.012	78.4	1.007
0.40	47.4	1.036	27.1	1.031	77.1	1.023
0.35	46.5	1.053	25.3	1.054	79.5	1.039
0.30	44.5	1.076	24.4	1.084	71.1	1.058
0.25	42.7	1.105	22.9	1.118	66.8	1.092
0.20	39.4	1.134	21.3	1.164	56.8	1.131
k (s^{-1})	48.3 ± 5.2		28.0 ± 3.8		73.0 ± 7.4	

[a] In solvent containing Et_4NBF_4 (0.1 M) and substrate (1.0 mM) at 313.2 K. The analysis and the theoretical data are from ref 22.

The conclusion from the discussion above is that the overall reactions are mixed eC–eCe_h processes but that the data obtained during kinetic experiments fit the eCe_h mechanism better. For this reason, rate constants were evaluated with use of theoretical data for the eCe_h mechanism for both DPSC and DCV studies. It should be emphasized that only the numerical values of rate constants are affected by the eC–eCe_h uncertainty. The rate law, i.e., reaction orders, or activation energies are unaffected. The possible error involved contributes to uncertainty only in the entropy of activation, a quantity that is normally associated with considerable error.

The rate constants evaluated from DPSC data (Table VII) with R_I ranging from 0.750 to 0.200 had standard deviations of the order of ±10%. The rate constants evaluated by DCV under the same conditions were nearly identical for the reactions of $7^{\bullet+}$ and $8^{\bullet+}$ but differed by nearly a factor of 2 for the reactions of $9^{\bullet+}$. Assuming competitive eC and eCe_h pathways with equal contributions of the two results in rate constants for the decomposition of $9^{\bullet+}$ in acetonitrile at 313.2 K equal to 133 s^{-1} (DPSC) and 129 s^{-1} (DCV).

The Products of the Oxidation of 7, 8, and 9. Preparative oxidations were carried out at a platinum gauze cathode in a divided cell under constant current conditions. The current density with a large cathode (ca. 50 cm^2) was sufficiently small so that the potential of the working electrode remained well below the reversible potentials for the oxidations for more than 90% conversion of substrates. The electrolyses were conducted at a high temperature, 333 K, to minimize the contribution of second-order processes. The temperature effect data presented in a previous section show that all three cation radicals undergo first-order reactions under these conditions.

During preparative scale oxidations the anode compartment was equipped with microelectrodes so that the disappearance of the diazo compound could be monitored amperometrically at 20-s intervals throughout the electrolysis. Over most of the course of

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(22) Parker, V. D. *Acta Chem. Scand.* **1984**, *A38*, 671.

Table VIII. Rate and Activation Parameters for the Decomposition of Diazoalkane Cation Radicals

solvent	substrate	**7**	**8**	**9**
CH_3OH	$k_{313.2}$ (DCV) (s^{-1})	33.2	17.6	148
	E_a (kcal/mol)	16.5	15.9	16.2
	$\Delta H^{\ddagger}$ (kcal/mol)	15.9	15.3	15.6
	$\Delta S^{\ddagger}_{313.2}$ (cal/(K·mol))	−1.0	−4.2	+1.0
CH_3CN	$k_{313.2}$ (DCV) (s^{-1})	46.3	29.7	129
	$k_{313.2}$ (DPSC) (s^{-1})	46.3	29.0	133
	E_a (kcal/mol)	15.5	16.6	16.2
	$\Delta H^{\ddagger}$ (kcal/mol)	14.9	16.0	15.6
	$\Delta S^{\ddagger}_{313.2}$ (cal/(K·mol))	−3.5	−0.9	+0.8

Table IX. Products (%)[a] of Constant Current Electrooxidation of **7**, **8**, and **9** in Methanol Solution at 60 °C

	diazoalkane		
products	**7**	**8**	**9**
Ar_2CHOMe	32.2	3.2	56.6
$Ar_2C{=}O$	53.6	24.5[b]	7.1
$Ar_2C(OMe)_2$	n.d.	61.4[b]	30.2
other identified products	$PhCO_2Me$ 2.7 $Ph_2C{=}CPH_2$ 7.9 $(Ph_2CH)_2$ 1.7	$C_{17}H_{16}O_3$ 6.7	$C_{15}H_{12}$ 1.4
n_{app}	1.7_6	1.9_8	1.2_3

[a] Uncorrected for FID response; the figures refer to percentage of diazoalkane converted into each product. [b] Approximate ratio confirmed by ^1H NMR spectroscopy (90 MHz).

the reactions, the decrease in the diazoalkane concentration showed a linear dependence on time (Faradays passed). The diazoalkane concentration, in $CH_3OH/NaClO_4$ (0.1 M) containing excess pyridine (10–60 mM), was ca. 2.5 mM in the case of **7** and **9**, but for **8** this was increased to 25 mM. Electrolyses were carried to completion and the contents of the anode compartment partitioned between water and dichloromethane. Analysis was by gas chromatography, identification being by comparison of retention times with those of authentic specimens and/or mass spectrometry.

Table IX summarizes the results. The products in each case account for more than 95% of the initial diazo compound; other products, of which there were several, especially in the case of **8**, could not be unambiguously identified but individually amounted to no more than 0.5% of the total product. Some of these products were evidently more highly oxidized than the main products, but the presence of $Ph_2C{=}CPh_2$ may indicate some small contribution from proton-catalyzed decompostion in the late stages of reaction of **7**. Approximate n values are indicated also in Table IX. All three values lie between 1 and 2, confirming the mixed eC/eCe_h nature of the electrolyses. We call attention to the inverse correlation of the percentage of methyl ether produced with n_{app}.

Preparative experiments were conducted in CH_3CN as solvent at 298 K in the presence of MeOH and 2,6-lutidine. In these cases, complex mixtures of products were formed, HPLC analysis indicating the presence of at least 18 components in one run. Substantial quantities of very involatile materials that could not be identified by GC/mass spectrometry were present.

Discussion

The experimental observations may be summarized as follows:

(i) All three diazoalkanes undergo electrooxidation in a nonchain process in the presence of pyridine bases; n values lie between 1 and 2.

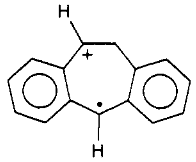
(ii) The rate of disappearance of the diazoalkane cation radical is first order in cation radical and the rate shows little dependence on the solvent (CH_3CN–MeOH) composition and is independent of the nature or concentration of nucleophilies and of the isotopic composition of the solvent. Only small kinetic effects result from changes of the supporting electrolyte.

(iii) At temperatures >300 K where reactions of higher order than 1 do not compete, the reactions show quite high activation energies (ca. 16 kcal·mol^{-1}) with entropies of activation close to 0.

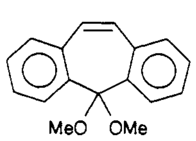
(iv) In the highly nucleophilic solvent methanol most of the diazoalkane is converted into three products: the related methyl ether, ketone, and dimethyl ketal.

The Rate-Limiting Step. We believe that this evidence indicates unambiguously that in all three cases the heterogeneously generated diazoalkane cation radical undergoes unimolecular loss of dinitrogen to produce the corresponding carbene cation radical. At temperatures above ambient, there is no evidence that the diazoalkane cation radicals dimerize, as was the case with the cation radical of 9-diazofluorene,[14] or react with nucleophiles, even ones as abundant as solvent methanol. Thus the rates of consumption of $R_2CN_2^{\bullet+}$ are affected little by the composition of solvent mixtures of acetonitrile and methanol, solvents of rather similar dielectric constant but widely different nucleophilicity. Nor is there evidence of hydrogen abstraction from the solvent by $R_2CN_2^{\bullet+}$; indeed the kinetic effects of changing from CH_3OH to CD_3OD are so small as to exclude not only this pathway but also probably direct nucleophilic solvent participation in the rate-limiting step. It is remarkable that these relatively long-lived diazoalkane cation radicals are not apparently susceptible to nucleophilic attack by methanol or even pyridine at moderate concentrations. The apparently low reactivity of some cation radicals[23] has been a matter for much discussion in the past and has prompted qualitative theoretical speculation recently.[24] However, the contention that cation radicals are generally of low reactivity toward nucleophiles has been challenged.[25] For example, reactions of 9-phenylanthracene cation radical with nitrogen-centered nucleophiles can take place at nearly diffusion controlled rates.

Unimolecular cleavage of the carbon-to-nitrogen bond in $R_2CN_2^{\bullet+}$ appears to be the only possibility. The activation parameters are very similar to those observed for carbene anion radical formation in systems where charge dissipation within the hydrocarbon moiety is substantial and the structures of **7**, **8**, and **9** are all capable of delocalization of positive charge as judged by the stabilities of the carbenium ions R_2CH^+. In the case of $\mathbf{8}^{\bullet+}$, molecular modelling suggests the possibility of an intramolecular hydride transfer concerted with nitrogen loss to give the intermediate cation radical **12**, a process that would circumvent carbene cation radical formation. The close similarity of the kinetic parameters for $\mathbf{8}^{\bullet+}$ to those for $\mathbf{7}^{\bullet+}$ and $\mathbf{9}^{\bullet+}$ argues strongly against such a pathway and for reaction by way of the carbene cation radical in all three cases. Moreover no products obviously derived from **12** could be found in preparative oxidations of **8**, the nearest being a trace of **13**.



12



13

In passing from $\mathbf{8}^{\bullet+}$, the slowest reacting, to $\mathbf{9}^{\bullet+}$ the fastest, it is to be noted that there is only a modest rate variation of ca. ninefold in CH_3OH and fourfold in CH_3CN. Taking pK_{R^+} for R_2CH^+ as a measure of the ability of the carbene framework to support the positive charge suggests that the rate is only very weakly dependent on this property. With use of Looker's values[26] of pK_{R^+} for the carbenium ion corresponding to $\mathbf{7}^{\bullet+}$ (−13.3), $\mathbf{8}^{\bullet+}$ (−8.0), and $\mathbf{9}^{\bullet+}$ (−3.7), it is evident that no general correlation exists. It should be remembered, however, that while the stereoelectronic situations around the CN_2 group in **8** and **9** are

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[23] Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55. Bard, A. J.; Ledwith, A.; Shine, H. J. *Ibid.* **1975**, *13*, 155.

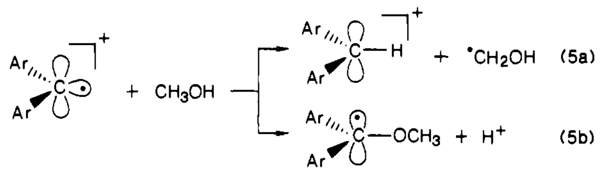
[24] Pross, A. *J. Am. Chem. Soc.* **1986**, *108*, 3537.

[25] Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1987**, *109*, 2521.

[26] Looker, J. I. *J. Org. Chem.* **1968**, *33*, 1304. See also: Olah, G. A.; Liang, G. *Ibid.* **1975**, *41*, 2108.

probably rather similar, that in **7** is different by virtue of the possibility of rotation about the Ph–CN_2 bonds. For this reason it may be anticipated that N_2 loss from $\mathbf{7}^{\bullet+}$ will be quicker than expected on the basis of pK_{R^+}; by analogy with the situation in the thermolysis of Ph_2CN_2 giving the carbene,[27] and assuming that the transition state for N_2 loss from $\mathbf{7}^{\bullet+}$ is close in structure to the carbene cation radical, one phenyl group should be capable of π-delocalization of the positive charge while the other, roughly orthogonal to the first, can stabilize the unpaired electron. A more realistic estimate of the sensitivity of N_2 loss from diazoalkane cation radicals to positive charge delocalization comes from the rate constants for $\mathbf{8}^{\bullet+}$ and $\mathbf{9}^{\bullet+}$; the Brønsted-type exponents log $k_{313.3}/pK_{R^+}$ are 0.21 (CH_3OH) and 0.15 (CH_3CN).

Reaction Pathways of Carbene Cation Radicals. The evidence from both the kinetic investigation and the preparative experiments conducted under conditions of constant current electrolysis is that oxidations of **7**, **8**, and **9** take place by competing one- and two-electron pathways. Compound **8** comes close to pure two-electron oxidation and **9** gives the highest proportion of one-electron oxidation. The implication of this competitive situation is that the product of the rate-limiting step, the carbene cation radical, shows the behavior both of a radical (eC-behavior) and of an electrophile (eCe_h behavior) toward available reaction partners, of which the solvent is the most abundant; this is illustrated in eq 5a and 5b. Thereafter, the reaction pathways will depend on the reactivity of the carbenium ion and radicals produced, carbenium ions reacting further with solvent most probably, and α-methoxy radicals by a further one-electron oxidation step (eCe_h) to give the corresponding cation rather than by dimerization. Pathway 5b can also give rise to eC behavior if hydrogen atom abstraction by the α-methoxy radicals can compete with the homogeneous electron transfer. The principal products of reaction in the presence of methanol are thus expected to be Ar_2CHOCH_3 mainly from the eC pathway and $Ar_2C(OCH_3)_2$ from the eCe_h pathway. Such products are indeed formed. The closely related diazo compounds **8** and **9** give rise to both types of product but in interestingly different proportions; the ratio of $Ar_2CHOCH_3/Ar_2C(OCH_3)_2$ is around 0.05 from **8** but about 1.9 for **9** which might be expected to favor the eC pathway since it would preserve the tropylium-type delocalization of the positive charge which would be lost on reaction with a nucleophile.



Ketones, are, however, substantial products from all three diazo compounds, and, in the case of **7**, benzophenone is the major product with none of the ketal being detected. It seems unlikely that this is an artefact of the analytical procedure, since the ketones were detectable spectroscopically in the reaction mixtures before analysis and the most probable precursors, the ketals, are stable under basic conditions such as were maintained during the aqueous workup. It would seem that the ketone, which is at the same oxidation level as the ketal, is a major product of the eCe_h pathway rather than the result of reaction of, for example, radical intermediates with adventitious oxygen. A possible pathway might be by nucleophilic displacement at the methoxy carbon of the α-methoxycarbenium ion (eq 6), but proof of this would require a more detailed examination.

$$Ar_2C^+—OCH_3 + Nu \rightarrow Ar_2C{=}O + CH_3Nu^+ \qquad (6)$$

The chemical behavior of these systems gives little evidence for the participation of the corresponding electrically neutral carbenes. Such species would be expected to react with methanol to give Ar_2CHOCH_3 at rates close to diffusion control. In order for carbenes to be formed, the carbene cation radicals would have to acquire an additional electron and the most easily oxidized species in the reaction mixtures is the parent diazoalkane. Significant involvement of carbenes would then be signalled by an n value less than unity, since the decomposition of the diazoalkane would be a chain process, and by a high yield of Ar_2CHOMe. While the oxidation of **9** gives the corresponding methyl ether as the main product and shows the lowest n value of the three diazo compounds studied, n is still substantially greater than unity and, as already discussed, there are good electronic reasons why the eC mechanism would be favored in this case. Furthermore, the preparative experiment on **8** was done at a tenfold higher substrate concentration than the experiments on **7** and **9**. The higher concentration should have favored the chain process yet the highest value of n and lowest yield of methyl ether resulted.

There are good reasons, based on our present results, for not expecting carbene-mediated decomposition in these systems. The activation parameters for thermolysis of **7** in CH_3CN solution are $\Delta H^\ddagger = 27.2$ kcal/mol, $\Delta S^\ddagger = 0$.[28] For the corresponding cation radical of **7**, $\Delta H^\ddagger = 14.9$ kcal/mol, $\Delta S^\ddagger = -3.5$ cal/(K·mol). Assuming that the transition states for loss of dinitrogen from these species are close in energy to the corresponding intermediates, the carbene and carbene cation radical, then at 333.2 K eq 7 holds.

$$\Delta G(Ph_2C^{\bullet+}–Ph_2C:) = \Delta G(Ph_2CN_2^{\bullet+}–Ph_2CN_2) - 11.1 \text{ kcal/mol} \qquad (7)$$

It is evident that the process $Ph_2C^{\bullet+} + Ph_2CN_2 \rightarrow Ph_2C: + Ph_2CN_2^{\bullet+}$ is thermodynamically unfavorable and would be unlikely to compete with the alternative processes in (5).

In oxidations of all three diazo compounds evidence was found in the GC/MS results for small amounts of products oxidized to a higher level than that of the ketone; examples are the formation of methylbenzoate from **7**, of **13** from **8**, and of anthraquinone from **9**. This leads us to suppose that a varied chemistry may be available. Indeed the complexity of the product mixture derived from **7** on oxidation in CH_3CN containing 1 M methanol supports this view and suggests that carbene cation radicals react rather indiscriminately under circumstances other than those described here.

Conclusions

In this paper we have presented evidence that anodic oxidation of three diaryldiazoalkanes of rather closely related structure leads to the corresponding cation radicals which are sufficiently unreactive toward nucleophiles in the solvent that they undergo unimolecular decomposition. It has been argued that this process is the loss of molecular nitrogen giving rise to the corresponding carbene cation radical. It thus appears that these intermediates are much more readily accessible than might have been thought. They show a pattern of reactivity that exhibits both electrophilic and radical-like facets. Work is in hand on other systems to investigate the diversity of chemical behavior of these intriguing species.

Experimental Section

Materials. Diazo Compounds. Diazodiphenylmethane (**7**) was prepared by oxidation of benzophenone hydrazone,[29] mp 29 °C (dec). The cyclic diazo compounds **8** [mp 71 °C dec] and **9** [mp 62 °C dec] were prepared from the corresponding ketones by way of the tosylhydrazone with use of the method of Moritani et al.[30] The purity of the compounds was checked by treatment with HBF_4 in methanol and with acetic acid in acetonitrile solution. GLC analysis then confirmed the formation of a single product, the corresponding methyl ethers or acetate esters, in each case.

Solvents and Supporting Electrolytes. These were the purest available commercial materials and were used without further purification. Likewise pyridine and 2,6-lutidine were pure commercial samples

Electrochemical Kinetic Studies. The cells, instrumentation, and measurement procedures were as used in our previous investigations on

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diazo compounds and have been described elsewhere.[31]

Preparative Experiments. These were carried out in H-shaped cells divided by a glass frit and fitted with platinum gauze anode and cathode. The procedures for electrolysis and monitoring of the residual diazoalkane concentration were as recently described.[18]

Product solutions were worked up by pouring into water (250 cm^3) and extracting with CH_2Cl_2 (2 × 50 cm^3). The extracts were washed with water, dried (Na_2SO_4), and evaporated to dryness in vacuo. Analysis was by GLC and GLC/MS with a VG 7070E instrument. GLC conditions were 25 m capillary column (i.d., 0.3 mm); stationary phase, OV1; temperature program 80–250 °C at 10 °C/min. Identification was from retention times, and the mass spectra which whenever possible were compared with that of authentic specimens. A flame ionization detector was used for the quantitative analyses, the response being uncorrected since previous experience with compound **7** and its decomposition products indicated that responses per mole of **7** converted to each product were close to unity. In the case of electrolysis of **8** the scale was sufficient for ^{1}H NMR spectroscopic analysis to be attempted, but this was less successful than expected because of the coincidental identity of the chemical shifts of the methyl protons of the dimethyl ketal produced and the methylene protons of the ethano bridge. Integration of the signals and comparison with that for the aromatic protons gave an approximate confirmation of the ratio of ketal to ketone.

Registry No. **7**, 883-40-9; **7**$^{\cdot+}$, 64401-31-6; **8**, 6141-55-5; **8**$^{\cdot+}$, 109217-77-8; **9**, 6141-56-6; **9**$^{\bullet+}$, 109217-78-9.

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Many-Body Theory of the Ionization Energies of CH_3^-, SiH_3^-, and GeH_3^-

J. V. Ortiz

Contribution from the Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131. *Received February 24, 1987*

Abstract: Electron propagator theory is used to calculate the vertical ionization energies of CH_3^-, SiH_3^-, and GeH_3^-. Basis set augmentations are made until changes in the computational results are small. Adiabatic ionization energies are obtained via many-body-perturbation-theory calculations on the neutral potential energy surface. The adiabatic values are in excellent agreement with photoelectron spectroscopy measurements on CH_3^- and SiH_3^-. Comparable calculations are made for GeH_3^-. Calculated vertical ionization energies are 0.51 eV for CH_3^-, 1.79 eV for SiH_3^-, and 2.01 eV for GeH_3^-; adiabatic counterparts are 0.19, 1.31, and 1.39 eV, respectively. Calculations employing effective core potentials for SiH_3^- and GeH_3^- agree closely with all-electron results. Vertical ionization energies employing these techniques are 1.88 eV for SiH_3^- and 1.97 eV for GeH_3^-. Adiabatic effective core potential results are 1.46 eV for SiH_3^- and 1.49 eV for GeH_3^-.

I. Introduction

Electron affinities are important in many areas of chemistry, such as the behavior of anions in the gas phase and in solution.[1] Several physical techniques measure these quantities precisely, but accompanying structural information often is uncertain or incomplete. For example, unfavorable Franck–Condon factors may obscure the adiabatic electron binding energy in a photoionization experiment. With some methods, it may be necessary to report just an upper bound. At this point, theory can provide the missing geometries and distinguish between vertical and adiabatic electron affinities.

It is well known that there are substantial nuclear rearrangements accompanying the removal of an electron from the methyl, silyl, and germyl anions.[2] The neutrals have less pyramidal and more planar structures than the anions. Anion photoelectron spectroscopy can yield some information on the neutral by interpreting final state vibrational structure.[3,4] Isotopic substitutions cause larger shifts in some vibrational final states than in others, and inferences on which peak represents the adiabatic ionization energy can be drawn. Methide and silide adiabatic ionization energies are determined in this way, but for the germide species, the picture is less complete. Ion cyclotron resonance photodetachment spectra are available for the germyl anion, but the photoionization onsets are not sharp enough to definitively determine a vertical or adiabatic ionization energy.[5]

Many computational studies of these anions and neutrals have been undertaken.[2] Most have concentrated on minima in the potential energy surface and on barriers to inversion. Such investigations can generally be tackled on the Hartree–Fock level with double-ζ plus polarization basis sets, perhaps augmented with a set of diffuse functions for studying negatively charged species. Spacings between potential energy surfaces containing different numbers of electrons, however, will typically require a correlated treatment with multiply augmented and polarized basis sets.[6]

II. Methods

Vertical electron binding energies are currently calculated in two different ways: directly and indirectly. The former set of methods evaluates an energy difference in one calculation, while the latter set of methods requires subtraction of total energies for

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