tained by protonation at −60° of aromatic hydrocarbons in 11.5 ± 0.5 mole % SbF_5-HSO_3F. These correlate closely with similar values obtained by Mackor and coworkers[3] in liquid hydrogen fluoride at 0°. Hence thermodynamic properties for arenonium ion formation in our system are quite relevant to processes leading to these ions under very different conditions of medium and temperature.

There are a number of reasons why benzenonium ions were selected as the point of departure for a systematic study of the relationship between the structure and stability of carbonium ions. A wealth of nmr and other spectral data have established their clean, rapid formation in systems such as ours at low temperatures.[4,5] The necessary compounds are readily available in high purity, and there are no complications due to a leaving group. Brown and Melchiore[6] have shown that there is virtually no variation in the energy of π-complex formation for a series of polyalkylbenzenes, assuring us thereby that structural effects on ΔH_{obsd} reflect primarily changes in carbonium ion stability.

Figure 1 compares our calorimetric heats of carbonium ion formation (ΔH_{obsd}) in SbF_5-HSO_3F at −60° with those determined by Mackor[3] in HF-BF_3 at 0° using an ice calorimeter. Both sets of enthalpy data are plotted against $\Delta G_{\mathrm{C^+}}$, the free energy of arenonium ion formation in liquid HF-BF_3.[7] Linear relationships between free energies of protonation and rates of electrophilic substitution reactions are well documented.[4,10] Both plots in Figure 1 are good straight lines whose least-squares slopes agree within experimental error (1.0 ± 0.1 and 1.16 ± 0.08,[11] respectively, for Mackor's results and our data). Therefore, temperature and solvent effects on *relative* $\Delta H_{\mathrm{C^+}}$ values within this series of benzenonium ions are probably negligible.[12] Other examples of broad correlations between heats of ionization in one medium and free energies of ionization in another have been observed previously.[13]

All calorimetric measurements were repeated at least six times in a given batch of acid and many of the results include runs in different batches on different days. Relative errors (standard deviations) were 5% or less except for azulene (point 12) for which $\Delta H_{\mathrm{obsd}} = -32.3 \pm 3.0$ kcal/mole. Thus, all points are within their individual experimental errors of the correlation line with the exception of 8, hexamethylbenzene. It is probably significant that this is the only ion in the series with an alkyl group at the point of protonation.

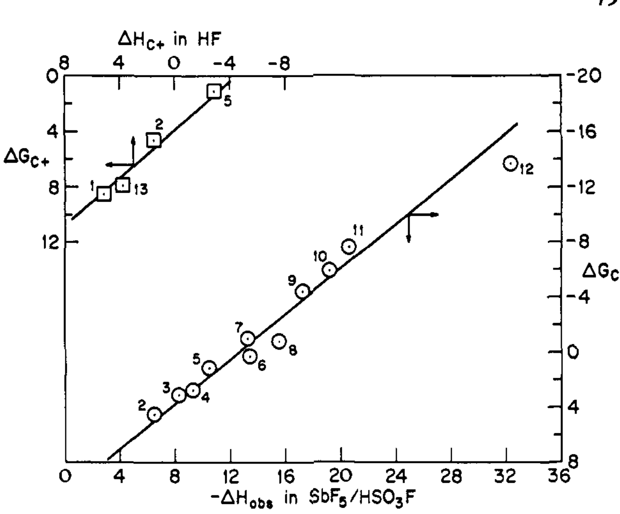

Figure 1. Correlation of heats of carbonium ion formation in SbF_5-HSO_3F at −60° and in HF-BF_3 at 0° with free energy of ionization in HF-BF_3 at 0°. Points correspond to ions derived from the following compounds: (1) toluene; (2) *m*-xylene; (3) 1,2,4,5-tetramethylbenzene; (4) 1,2,3,4-tetramethylbenzene; (5) 1,3,5-trimethylbenzene; (6) 1,2,3,5-tetramethylbenzene; (7) pentamethylbenzene; (8) hexamethylbenzene; (9) anthracene; (10) 2-methylanthracene; (11) 9,10-dimethylanthracene; (12) azulene; and (13) *p*-xylene.

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[3] E. L. Mackor, A. Hofstra, and J. H. Van der Waals, *Trans. Faraday Soc.*, **54**, 186 (1958).

[4] Reviewed by H. H. Perkampus, *Advan. Phys. Org. Chem.*, **4**, 195 (1966).

[5] Reviewed by G. A. Olah and M. W. Meyer in "Friedel Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 623 ff.

[6] H. C. Brown and J. J. Melchiore, *J. Am. Chem. Soc.*, **87**, 5269 (1965).

[7] These values were calculated from p*K* data corrected for symmetry factors.[4] With the exception of azulene (point 12), measured in aqueous perchloric acid[8] and extrapolated to HF by acidity functions, all p*K* values were determined in liquid HF-BF_3.[9]

[8] F. A. Long and J. Schulze, *J. Am. Chem. Soc.*, **86**, 327 (1964).

[9] E. L. Mackor, A. Hofstra, and J. H. Van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).

[10] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

[11] Point 12 (azulene) was not included in the determination of the slope.

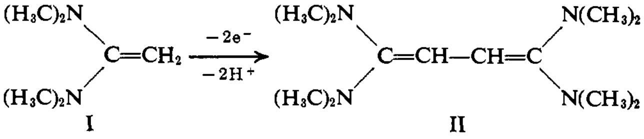
[12] Obviously there are large *absolute* differences between $\Delta H_{\mathrm{C^+}}$ in the two systems.

[13] E. M. Arnett and J. J. Burke, *J. Am. Chem. Soc.*, **88**, 4308 (1966).

Electrolytic Oxidations of Organics. I. Oxidative Coupling of Vinylidenebisdimethylamine to 1,1,4,4-Tetrakis(dimethylamino)butadiene[1]

Sir:

Interest has sharply increased in electrochemical oxidations of organics, primarily aromatics.[2] This interest has long been delayed because of the complexity of reactions subsequent to initial charge transfers. In the present paper we wish to report the observation of a major product, a butadiene, in the electrooxidation of a somewhat simple organic, an ethylene. We have observed that vinylidenebisdimethylamine[3] (I) can be oxidized elecrolytically to 1,1,4,4-tetrakis(di-



$$[(H_3C)_2N]_2C{=}CH_2 \xrightarrow[-2H^+]{-2e^-} [(H_3C)_2N]_2C{=}CH{-}CH{=}C[N(CH_3)_2]_2$$

I II

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[1] Presented at the 1967 Midwest Regional American Chemical Society Meeting, University of Missouri, Columbia, Mo., Nov 2-3, 1967.

[2] For example: (a) M. E. Peover in "Electroanalytical Chemistry," Vol. 2, A. J. Bard, Ed., Marcel Dekker, Inc., New York, N. Y., 1967; (b) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967); (c) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Am. Chem. Soc.*, **89**, 1752 (1967); (d) L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *ibid.*, **89**, 5766 (1967); (e) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *ibid.*, **88**, 3498 (1966); (f) L. Eberson and K. Nyberg, *ibid.*, **88**, 1686 (1966); and (g) L. L. Miller and A. K. Hoffman, *ibid.*, **89**, 593 (1967).

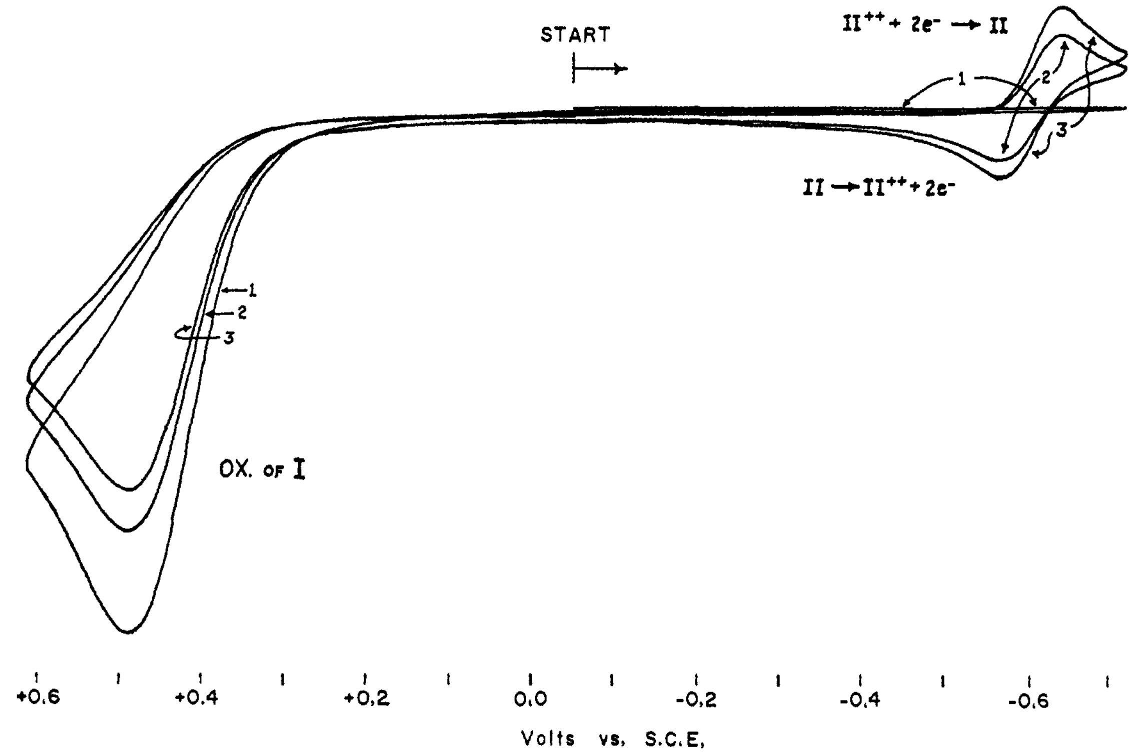

Figure 1. Cyclic voltammetry of compound I. The three initial scans are shown; the numbers indicate the successive scans.

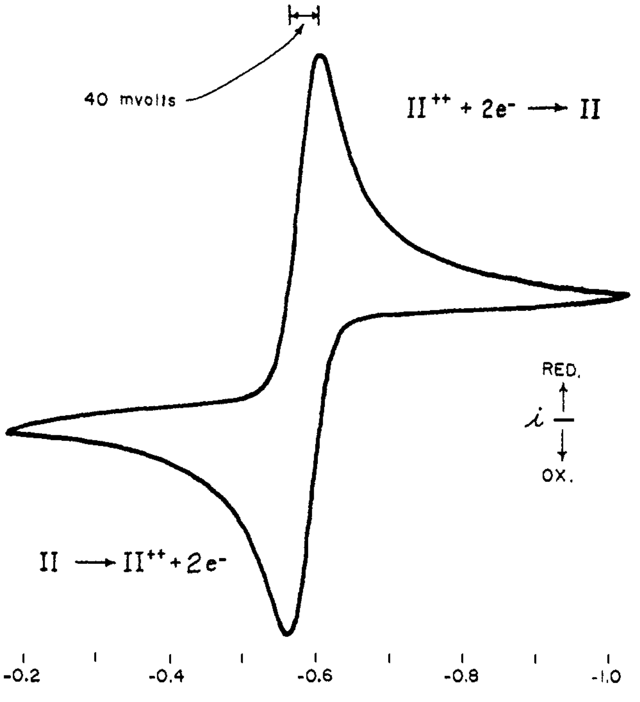

Figure 2. Cyclic voltammetry of compound II (steady state).

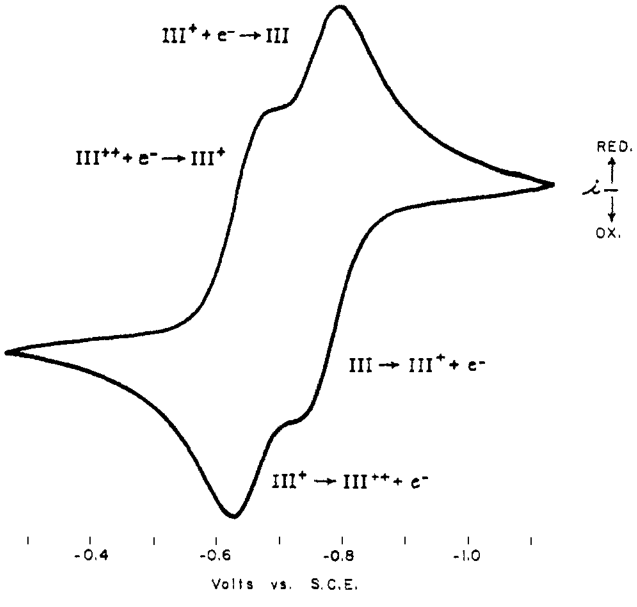

Figure 3. Cyclic voltammetry of compound III (steady state).

methylamino)butadiene[3] (II). This reaction is clearly demonstrated by cyclic voltammetry.[4] In Figure 1 we see the electrolysis of a *ca.* 3 m*M* solution of I in N,N-dimethylformamide containing 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte. The electrolysis was executed at a platinum disk sealed in glass. Note that (scan 1 in Figure 1) no species in the solution of I is oxidizable or reducible in the potential region of -0.7 to $+0.2$ v *vs.* the saturated calomel reference electrode (sce). However, on scanning to a more positive potential, oxidation of I takes place and this leads to formation of a product showing a reversible redox couple at -0.58 v *vs.* sce. This reversible couple is clearly assignable to II by (1) the exact agreement of potentials (see Figure 2) in a potential region devoid of other possibilities and (2) the reversibility. In Figure 1 the platinum electrode had been polarized at -0.05 v *vs.* sce and then scanned between -0.7 and $+0.6$ v several times to give the curves shown. In these

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(3) H. Weingarten and W. A. White, *J Org. Chem.*, **31**, 2874 (1966).

(4) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964), and references therein.

initial scans the current peaks due to the oxidation of I successively decrease in amplitude (due to exhaustion of I near the electrode), while those due to the redox couple of II increase (as the concentration of II builds up near the electrode). This demonstration of the oxidative coupling of I to form II is also observable in acetonitrile.

A surprising fact about the reversible redox couple for II is that it is a *two*-electron process. This was clearly demonstrated by cyclic coulometry. Closely related to this tetraaminobutadiene is tetrakis(dimethylamino)ethylene (III) which was studied extensively by Kuwata and Geske.[5] The cyclic voltammetry of III appears in Figure 3. Note that the two one-electron steps are separated by only 0.1 v for this compound.

We are presently studying the electrolytic oxidations of other aminoethylenes and of aromatic hydrocarbons and will report on these in the near future.

(5) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964).

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The Radiation-Induced "Hydrolysis" of the Peptide Bond[1]

Sir:

We find that the γ radiolysis of oxygen-free solutions of simple peptides such as the N-acetylamino acids leads to liberation of the free amino acid as a major reaction product. As a specific example, the alanine[2] yield from N-acetylalanine in an evacuated solution at pH 7 increases abruptly with increasing solute concentration over the range 0.05–0.25 *M* and then levels off to a limiting value of *G*(alanine) $\simeq$ 1 at acetylalanine concentrations above 0.5 *M* as shown in Figure 1.

This radiation-induced liberation of free amino acid is quenched by second solutes such as hydronium ion, molecular oxygen, and chloroacetate ion, all of which are known to be effective scavengers of the hydrated electron, e_{aq}^-, formed in the radiation-induced step[3,4]

$$H_2O \rightsquigarrow H_2O_2,\ H_2,\ OH,\ H^+,\ e_{aq}^- \qquad (1)$$

The effect of chloroacetate ion on *G*(alanine) from 1 *M* acetylalanine at pH 7 is shown in Figure 1, insert. The reciprocal-yield plot gives $k_2/k_3 = 1.9 \times 10^2$ for the ratio of the rate constants of the competing reactions

$$e_{aq}^- + RCl \longrightarrow R + Cl^- \qquad (2)$$

$$e_{aq}^- + RCONHCHR_2 \longrightarrow (RCONHCHR_2)^- \longrightarrow \text{products} \qquad (3)$$

This value is in good agreement with other measurements of the reactivity of e_{aq}^- toward these solutes.[5]

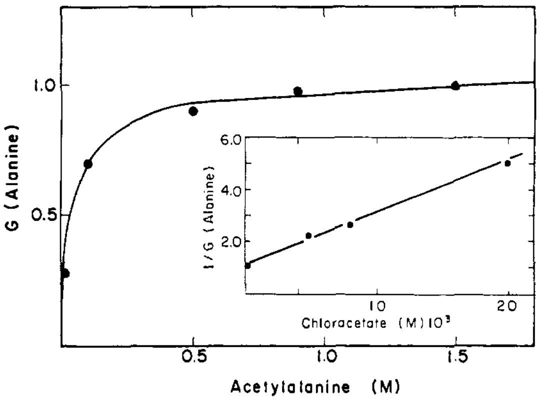

Figure 1. *G*(alanine) as a function of acetylalanine concentration in oxygen-free solution at pH 7 under γ rays. Insert: reciprocal yield plot of *G*(alanine) as a function of chloroacetate concentration in 1 *M* acetylalanine.

The evidence is then that the reducing species, e_{aq}^-, is specifically involved in the chemistry that leads to liberation of free alanine. Previous work has established that the oxidizing species, OH, is removed preferentially through H abstraction at the α-carbon position of acetylalanine

$$OH + RCONHCHR_2 \longrightarrow RCONH\dot{C}R_2 + H_2O \qquad (4)$$

where $k_4 = 2.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$.[6] Addition of an OH scavenger such as formate ion ($k_{f+OH} = 2.5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$)[4,7] at concentrations as high as 0.5 *M* has no effect on *G*(alanine) in 1 *M* acetylalanine.

Now, if the removal of e_{aq}^- *via* reaction 3 leads to reduction of the peptide linkage, *e.g.*

$$(RCONHCHR_2)^- + H_2O \longrightarrow R\dot{C}(OH)NHCHR_2 + OH^- \qquad (5)$$

then it is clear that combination of $R\dot{C}(OH)NHCHR_2$ with like species or with the α-carbon radical $RCONH\dot{C}R_2$ would lead to formation of Schiff-base derivatives of the type $R(R')C(OH)NHCHR_2$ which compounds are labile with respect to the decomposition

$$R(R')C(OH)NHCHR_2 \longrightarrow R(R')CO + NH_2CHR_2 \qquad (6)$$

The stoichiometry of reaction 6 would also be observed if the (Schiff base) radical $R\dot{C}(OH)NHCHR_2$ underwent the decomposition

$$R\dot{C}(OH)NHCHR_2 \longrightarrow R\dot{C}O + NH_2CHR_2 \qquad (7)$$

before dimerization. In any event, the main point here is that the formation of alanine through net reduction of the peptide linkage in accord with the stoichiometry of reactions 6 and 7 requires the concomitant formation of ketonic products R(R′)CO. Detailed chemical analyses[7] of the irradiated solutions reveal that the yield of such products is quite low with $G \leq 0.2$. Evidently reductive cleavage of the peptide bond does not yield the major part of the observed alanine even though the formation of this product is directly related to the attack of the reducing species, e_{aq}^-.

A concept that appears to provide a clue to the interpretation of the chemistry of the present system is that the radical products of e_{aq}^- and OH attack are subsequently removed not by dimerization (combination) but by disproportionation. Of course, disproportionation involving $R\dot{C}(OH)NHCHR_2$ and the α-carbon radical

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(1) This work was done under the auspices of the U. S. Atomic Energy Commission.

(2) Alanine was identified chromatographically and assayed by the ninhydrin method; since ammonia is produced as a minor product and is "ninhydrin positive," a correction was made on the basis of a standard ammonia assay after the method of Conway.

(3) C. J. Hochanadel and R. Casey [*Radiation Res.*, **25**, 198 (1965)] report the following 100-ev yield for reaction 1: $G_{OH} = 2.59$, $G_{e_{aq}^-} = 2.58$, $G_H = 0.55$, $G_{H_2} = 0.45$, $G_{H_2O_2} = 0.72$.

(4) For a recent compilation of rate data, see M. Anbar and P. Neta, *J. Appl. Radiation Isotopes*, **17**, 493 (1967).

(5) R. L. S. Willix and W. M. Garrison, *Radiation Res.*, **32**, 452(1967).

(6) M. A. J. Rodgers and W. M. Garrison, *J. Phys. Chem.*, in press.

(7) (a) B. M. Weeks, S. A. Cole, and W. M. Garrison, *ibid.*, **69**, 4131 (1965); (b) W. M. Garrison and B. M. Weeks, *Radiation Res. Suppl.*, **4**, 54 (1964); (c) H. L. Atkins, W. Bennett-Corniea, and W. M. Garrison, *J. Phys. Chem.*, **71**, 772 (1967).