The most interesting product isolated from the mixture, when methanol–liquid ammonia was used as the quenching agent, was identified as $CH_3OC(Ph)_2CH_2SbCl_4(NH_3)$. It formed colorless crystals, mp 158–160°.

*Anal.*[9] Calcd: C, 36.6; H, 3.66; N, 2.85; Cl, 28.9; Sb, 24.7. Found: C, 35.9; H, 3.78; N, 3.56; Cl, 28.8; Sb, 25.9. The presence of methoxy and phenyl groups was demonstrated by ir. The nmr spectrum (in $CF_3COCF_3$–$D_2O$) showed phenyl protons at $\delta$ 7.2, $CH_2$ protons at $\delta$ 3.8, and $OCH_3$ protons at $\delta$ 2.9 ppm. The integration led to the expected ratio 10:2:3, respectively.

The antimony compound was allowed to react in $CDCl_3$ with $SbCl_5$ at −60°. The nmr spectrum of the solution showed two signals at $\delta$ 8.1 and 5.3 ppm. The former corresponds to aromatic protons of the $Ph_2C^+$– group (see Table I) and the latter is assigned to $>C^+CH_2SbCl_4$. It seems that the presence of the $SbCl_4$ group shifts the methylene protons further downfield from the position (3.7 or 3.8 ppm) observed in $(Ph_2C^+CH_2)_2$ or in $Ph_2C^+CH_2CH_3$.

The isolation of the antimony compound indicates that two routes lead to formation of carbonium ions from $SbCl_5$ and olefin. $SbCl_5$ may act as an electron acceptor, as shown by eq 1, or it may disproportionate,[10] as $2SbCl_5 \rightleftarrows SbCl_4^+,SbCl_6^-$. The addition of $SbCl_4^+$ to the olefin leads to the formation of the carbonium ion. This mode of carbonium ion formation from an olefin and an electron acceptor will be further elucidated in the following communication.[11]

**Acknowledgment.** Financial support of this investigation by the National Science Foundation, by U. S. Air Force Contract AF-33(615)3788, and by the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

[9] Schwarzkopf Microanalytical Laboratories, New York, N. Y.

[10] L. Kolditz and H. Z. Preiss, *Z. Anorg. Allgem. Chem.*, 310, 242 (1961).

[11] S. Penczek, J. Jagur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, 90, 2174 (1968).

**B. E. Fleischfresser, W. J. Cheng, J. M. Pearson, M. Szwarc**
*Department of Chemistry, State University College of Forestry*
*Syracuse University, Syracuse, New York 13210*

*Received January 25, 1968*

---

## Formation of Carbonium Ions by Dissociative Electron Transfer

*Sir:*

Addition of tetranitromethane to 1,1-diphenylethylene in nitrobenzene (both components 1 *M*) produces instantaneously a new species, presumably a charge-transfer complex, which absorbs at $\lambda_{max}$ 410 m$\mu$. Assuming its extinction coefficient to be $10^3$–$10^4$, its equilibrium concentration was estimated to be about $10^{-3}$–$10^{-2}$ *M*. Apparently the complex decomposes slowly, the spectrum broadens, and eventually a new peak develops at $\lambda_{max}$ 385 m$\mu$. This reaction is accelerated by daylight and seems to be completed in about 12 hr.

The final product was isolated in the form of yellow crystals, mp 85.5°. It was identified as 1,1-diphenyl-2-nitroethylene. *Anal.* Calcd for $C_{14}H_{11}NO_2$: C, 74.5; H, 4.89; N, 6.25. Found: C, 74.3; H, 4.9; N, 6.24. This compound was described earlier,[1] mp 86–87°. The nmr spectrum of our product shows a sharp singlet at $\delta$ 7.51 and an aromatic band at $\delta$ 7.1–7.48 ppm. Integration gives a 1:10 ratio. The 7.51 ppm singlet is attributed to the $>C{=}CHNO_2$ proton. This assignment is justified because the analogous hydrogen in 2,4-dimethoxy-$\beta$-nitrostyrene[2] absorbs at $\delta$ 7.7 ppm. The presence of the $NO_2$ group was confirmed by ir (1340 and 1540 cm$^{-1}$).

The nmr spectrum of 1,1-diphenylethylene gives two sharp singlets at $\delta$ 5.42 (olefinic proton) and 7.4 ppm (aromatic protons). Hence, the kinetics of formation of the nitro compound in deuterated nitrobenzene may be followed by observing the decay of the 5.42-ppm line. On this basis, it was found that the conversion reached 70% after 7 hr.

These observations suggest the following mechanism.

$$Ph_2C{=}CH_2 + C(NO_2)_4 \rightleftharpoons \underset{\text{I}}{\text{charge-transfer complex}}\ \text{(rapid)} \qquad (1)$$

$$\text{I} \longrightarrow Ph_2C^+CH_2NO_2 + \overset{-}{C}(NO_2)_3 \qquad (2)$$

$$Ph_2C^+CH_2NO_2 + \overset{-}{C}(NO_2)_3 \longrightarrow Ph_2C{=}CHNO_2 + CH(NO_2)_3 \qquad (3)$$

Electron transfer to tetranitromethane results in dissociative capture.[3] Therefore, reactions 2 and 3 take place in a concerted manner, or the proton transfer takes place in the ion pair, and this accounts for the lack of dimerization.

To verify the existence of intermediate carbonium ion the reaction was reinvestigated in the presence of methanol. Under these conditions, as in the study of Schmidt, *et al.*,[4] the reaction yields the respective nitromethoxy derivative, *viz.*, $Ph_2C(OCH_3)CH_2NO_2$. This compound, previously described by Anschütz and Hilbert,[5] was isolated in nearly quantitative yield in the form of white crystals, mp 139.5°. *Anal.* Calcd for $C_{15}H_{15}NO_3$: C, 70.0; H, 5.81; N, 5.25. Found: C, 69.6; H, 5.9; N, 5.4. The nmr spectrum showed singlets at $\delta$ 7.8, 5.3, and 3.25 ppm in the ratio of about 10:2:3. Strong bands were seen in its ir spectrum, namely at 1555 and 1380 cm$^{-1}$, which characterize the aliphatic $NO_2$ or ONO groups,[6] and a less strong band at 1080 cm$^{-1}$, which indicates the presence of the C–O–R linkage. Since the compound is not solvolyzed when boiled with 97% formic acid,[7] it does not contain the ONO group.

It is obvious that the nitroethane derivative obtained in this experiment results from the carbonium ion $^+C(Ph)_2CH_2NO_2$. In the presence of methanol this ion is methoxylated and the proton from the hydroxyl group neutralizes the $^-C(NO_2)_3$ ion. In the absence of methanol the proton from the $>C^+CH_2NO_2$ group is transferred to $^-C(NO_2)_3$ and, therefore, the nitro olefin derivative is formed.

The proposed mechanism attributing the formation of the carbonium ion to the transfer of $NO_2^+$ group from tetranitromethane to olefin seems to be general.[8] This

[1] E. Beilstein, "Handbuch der organischen Chemie," Band 5, Springer Verlag, Berlin, 1930, p 1308.

[2] "Catalog of NMR Spectral Data," Varian Associates, Palo Alto, Calif., Spectrum No. 325.

[3] B. H. J. Bielski and A. O. Allen, *J. Phys. Chem.*, 71, 4545 (1967).

[4] E. Schmidt, R. Schumacher, N. Bäjor, and A. Wagner, *Ber.*, 55, 1753 (1922).

[5] R. Anschütz and A. Hilbert, *ibid.*, 57B, 1697 (1924).

[6] R. N. Haszeldine, *J. Chem. Soc.*, 2225 (1953).

[7] R. G. Pews, *J. Org. Chem.*, 32, 2914 (1967).

[8] J. M. Patterson, *ibid.*, 20, 1277 (1955).

is illustrated by the two examples quoted in the literature,[4] and another system of this kind was investigated in the course of our studies.

Interaction of tetranitromethane with $\alpha$-methylstyrene in deuterated methanol was followed by nmr. The spectrum of the original olefin eventually disappears and the new one shows a singlet at $\delta$ 4.65 ppm (attributed to the $CCH_2NO_2$ protons), a singlet at $\delta$ 1.75 ppm corresponding to the $CH_3$ protons which originally absorbed at 2.11 ppm, and a band centered at $\delta$ 7.4 ppm arising from the aromatic protons. The latter coincides with that observed in the original olefin. This assignment was confirmed by integration. During the course of the reaction the sum of both types of $CH_3$ protons remained in a constant ratio to the sum of the aromatic protons, and a similar relation held for the protons associated with the $\beta$ carbon. The conversion of $\alpha$-methylstyrene to the nitro compound is, therefore, quantitative.

Further evidence for the formation of carbonium ions in the reaction of tetranitromethane with olefins comes from studies of polymerization of oxetane initiated by this system. This cyclic ether is readily polymerized by cationic initiators but not by tetranitromethane alone. For example, no polymerization takes place in the system containing 1 *M* oxetane and 0.1 *M* tetranitromethane in nitrobenzene. On the other hand, polymerization of oxetane ensues when 1,1-diphenylethylene is added to the mixture of the ether and tetranitromethane in nitrobenzene. Obviously the intermediate carbonium ions formed in this system by the $NO_2^+$ transfer are responsible for the polymerization.

The transfer of $NO_2^+$ to the $\beta$-carbon atom of olefin, as shown in eq 2, is amply demonstrated. On the other hand, the transfer to aromatic rings does not take place. This was proved by the absence of polymerization when biphenyl, anthracene, or benzophenone (1 *M*) was added to the solution of oxetane (1 *M*) and tetranitromethane (0.1 *M*) in nitrobenzene.

**Acknowledgment.** Financial support of this investigation by the National Science Foundation, by U. S. Air Force Contract AF-33(615)3788, and by the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

**S. Penczek, J. Jagur-Grodzinski, M. Szwarc**
*Department of Chemistry, State University College of Forestry*
*Syracuse University, Syracuse, New York 13210*

*Received January 25, 1968*

## Effect of Solvation on the Reactivity of Ion Pairs

*Sir:*

At least two types of growing species, *viz.* ion pairs and free ions, participate in anionic polymerization carried out in certain ethereal solvents.[1-7] Furthermore, recent investigations[2,3] revealed that two types of ion pairs may contribute to propagation: the relatively inert contact pairs and the highly reactive solvent-separated pairs.

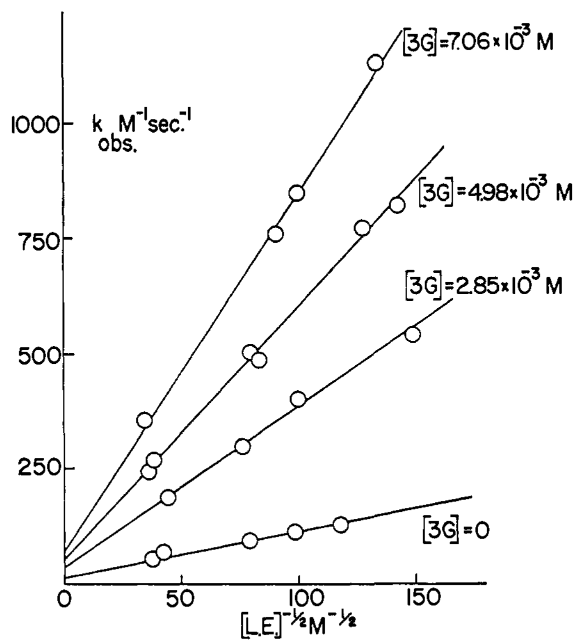

Figure 1. Linear dependence of propagation constant, $k_{obsd}$, of $\sim\!\sim S^-,Na^+$ polymerization on $1/[LP]^{1/2}$ at various concentrations of triglyme, 3G: solvent tetrahydropyran, 25°.

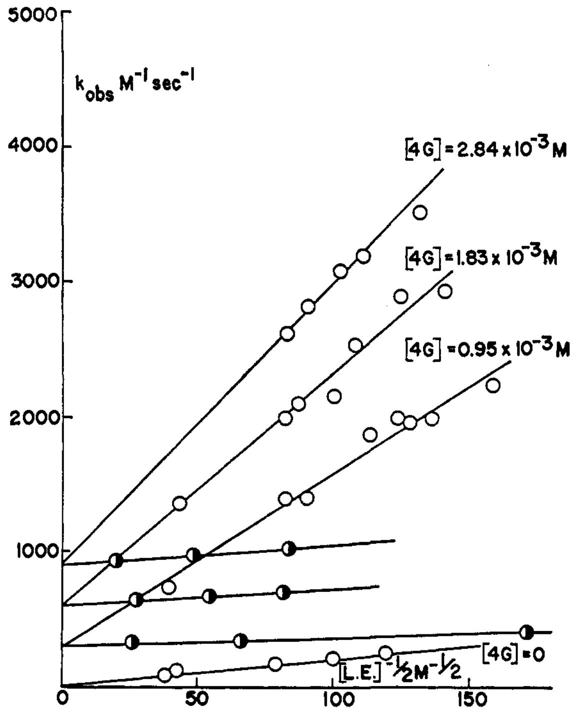

Figure 2. Linear dependence of propagation constant, $k_{obsd}$, of $\sim\!\sim S^-,Na^+$ polymerization on $1/[LP]^{1/2}$: solvent tetrahydropyran, 25°, in the absence and presence of tetraglyme. The half-shadowed points represent experiments performed in the presence of $Na^+$, $BPh_4^-$ which depresses the ionic dissociation of the living polymer and thus facilitates the determination of the intercept.

---

(1) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *Polymer*, **5**, 54 (1964); *J. Phys. Chem.*, **69**, 612 (1965).

(2) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **89**, 796 (1967).

(3) T. Shimomura, J. Smid, and M. Szwarc, *ibid.*, **89**, 5743 (1967).

(4) M. Fisher, M. Van Beylen, J. Smid, and M. Szwarc, submitted for publication.

(5) (a) H. Hostalka, R. V. Figini, and G. V. Schulz, *Makromol. Chem.*, 71, 198 (1964); (b) H. Hostalka and G. V. Schulz, *Z. Physik. Chem.* (Frankfurt), **45**, 286 (1965).

(6) W. K. R. Barnikol and G. V. Schulz, *Makromol. Chem.*, **86**, 298 (1965); *Z. Physik. Chem.* (Frankfurt), **47**, 89 (1965).

(7) J. Comyn, F. S. Dainton, G. A. Harpell, K. M. Hui, and K. J. Ivin, *Polymer Letters*, **5**, 965 (1967).