Table II. Isotopic Exchange between Nitro-Substituted Triphenylmethyl Chlorides and Labeled (^{36}Cl) Tetraethylammonium Chloride in Acetone at 80°

R	Total salt, M^a	10^6k_1, sec^{-1}	10^4k_2, M^{-1} sec^{-1}
$(p\text{-}NO_2C_6H_4)_3C$–	0.01	0.0 ± 0.07	10.6 ± 0.13
	0.10	0.32 ± 0.09	3.65 ± 0.16
	0.01^b	0.46 ± 0.04	2.60 ± 0.06
$(p\text{-}NO_2C_6H_4)_2C_6H_5C$–	0.01	0.5 ± 0.2	18.9 ± 0.4
	0.10	3.46 ± 0.05	12.1 ± 0.1

^{a} M = [Et_4NCl] + [Et_4NClO_4]. ^{b} Acetonitrile.

In the tri-*p*-nitro substrate the value of k_2 is reduced by a factor of three in going from 0.01 to 0.1 M electrolyte, nearly the same factor which is observed for a substrate, *p*-nitrobenzyl chloride, which undergoes a *bona fide* bimolecular substitution.[7] Thus the second-order term arises from a path which includes the nucleophile in the rate-determining transition state. In view of the particular nature of the substrates, several processes can be envisioned: (1) a one-step direct displacement on the central carbon atom; (2) a two-step process involving a slow displacement on an ion pair formed in a preliminary fast equilibrium

$$RCl \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R^+Cl^- \qquad \text{fast}$$

$$^*Cl^- + R^+Cl^- \overset{k_2'}{\rightleftarrows} R^{+*}Cl^- + Cl^- \qquad \text{slow}$$

(3) a two-step process involving the slow attack by chloride on the chlorine atom of the substrate

$$R{-}Cl + {}^*Cl^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftarrows}} R^- + ClCl^*$$

followed by a fast back reaction which may occur on either chlorine;[8] (4) a two-step process involving slow attack by chloride on chlorine to give a radical pair

$$RCl + {}^*Cl^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftarrows}} R\cdot + {}^*ClCl\cdot^-$$

followed by a fast recombination reaction.[8]

Mechanism 4 is proposed in view of the recent findings of Kornblum and co-workers.[9] However, *m*-dinitrobenzene[9] up to a molar ratio 5:1 produces no significant decrease of the rate, indicating that this mechanism does not contribute appreciably in the present case.

Mechanism 3 is suggested in view of the great stability associated with nitro-substituted triphenylmethyl carbanions. However, it can be dismissed in the present case since the structural effect on k_2 would predict the tri-*p*-nitro compound to react faster than the di-*p*-nitro one, while in fact it does not (Table II).

Of the two remaining possibilities we believe, at least for the trinitro substrate, a choice can be made in favor of 1 against 2.[10] This is based on the salt and solvent effects which are in agreement with mechanism 1 and opposite to what one can reasonably guess for mechanism 2. The transition state of the latter would in fact resemble an ion triplet, $Cl^-R^+Cl^-$, the stability of which, relative to the initial state, is expected to be favored by an increased polarity of the medium.[11] The structural effect is not inconsistent with mechanism 1 since bond breaking may well be predominant in these bimolecular substitutions.[5b]

Besides the medium effects, the great reactivity of azide relative to chloride ion offers a strong argument for mechanism 1 against 2. The latter, owing to the ion-triplet character of the transition state, would be expected to exert little discrimination between different nucleophiles. Instead, tri-*p*-nitrotriphenylmethyl chloride appears to discriminate strongly between azide and chloride ions, k_{N_3}-k_{Cl^-} being about 500.

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[7] The pertinent data are (U. Miotti, unpublished results): acetone; 25°; *p*-nitrobenzyl chloride 0.01 M, $Et_4N^{36}Cl$ 1.04 × 10^{-3} M, and Et_4NClO_4 9.0 × 10^{-3} M, $k_2 = 9.13 \times 10^{-3}$ M^{-1} sec^{-1}; $Et_4N^{36}Cl$ 1.28 × 10^{-3} M and Et_4NClO_4 98.9 × $10^{-3}M$, $k_2 = 4.08 \times 10^{-3}$ M^{-1} sec^{-1}.

[8] Although in both mechanisms 3 and 4 the species at the right-hand-side have been written as being separated, the back reaction could conceivably occur while the product species have not yet diffused away and are contained in the same solvent cage.

[9] R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **87**, 4520 (1965).

[10] H. Weiner and R. A. Sneen, *ibid.*, **87**, 292 (1965), have presented suggestive albeit not conclusive evidence for the operation of mechanism 2 in the reaction of 2-octyl mesylate in aqueous dioxane.

[11] Another way, perhaps more convincing, of saying the same thing is that in mechanism 2 the observed second-order rate coefficient is compounded of an equilibrium constant for ion-pair formation ($K = k_1/k_{-1}$) and of a rate constant, k_2', for direct displacement on an ion pair, $k_2 = Kk_2'$. Then the observed salt and solvent effect would result from the combination of the effects on K (large increase with increasing polarity) and k_2' (small decrease with increasing polarity).

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Nondissociative Electron Attachment Reactions in γ Radiolysis of Solutions of Cyclic Perfluorocarbons in Alkanes

Sir:

Recently considerable attention has been given to the role of halogenated hydrocarbons as electron scavengers in systems undergoing radiolysis. Pulsed radiolysis of aqueous solutions has been used to establish the rates of reaction of hydrated electrons in the alkyl halides[1] and monohaloacetates.[2] Hamill[3] and his co-workers have studied the electron-capturing ability of several halogen- and acetoxy-substituted hydrocarbons in organic glasses undergoing radiolysis. Evidence has been obtained for electron capture by the solutes in all those cases where the electron affinity of the halogen or acetoxy group exceeded the bond dissociation energy of the carbon–halogen or carbon–acetoxy bond.[3d] In the liquid-phase radiolysis of CCl_4 and $CHCl_3$ solution in cyclohexane, the decrease in hydrogen yield was attributed by Stone and Dyne[4] to either excitation energy transfer or electron capture by solute.

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[1] A. Szutka, J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, **69**, 289 (1965).

[2] M. Anbar and E. J. Hart, *ibid.*, **69**, 271 (1965).

[3] (a) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962); (b) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962); (c) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, **36**, 169 (1963); (d) J. B. Gallivan and W. H. Hamill, *Trans. Faraday Soc.*, **61**, 1960 (1965).

[4] J. A. Stone and P. J. Dyne, *Can. J. Chem.*, **42**, 669 (1964).

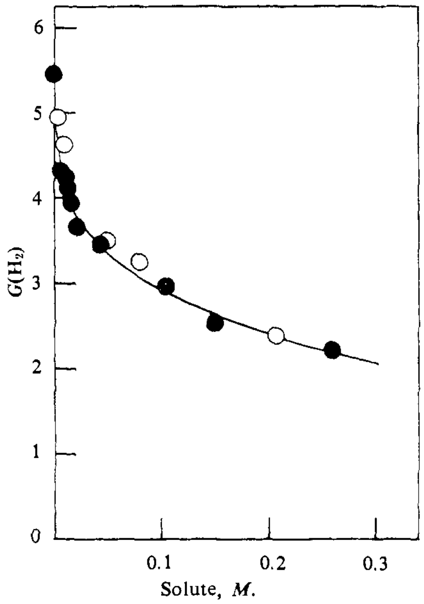

Figure 1. Plot of $G(H_2)$ in cyclohexane solutions *vs.* concentration of CCl_4 and perfluorocyclobutane. The values for CCl_4 were taken from Stone and Dyne.[4] (—●—●—●—) Perfluorocyclobutane; (—○—○—○—) carbon tetrachloride.

In this communication we wish to report the effect of low concentration of several perfluorocarbons on the hydrogen yield of γ-radiolyzed *n*-hexane and cyclohexane. Perfluorocarbons were chosen as additives on the assumption that some of them may have high reactivity toward thermal electrons. This assumption was based on the very high response of the electron capture detector toward several perfluorocyclocarbons[5] and the high dielectric strength of perfluorocyclobenzene and perfluoromethylcyclohexane.[6] Both these facts are consistent with the efficiency of removal by these compounds of electrons of low energy from an electron stream.

Deaerated dilute solutions of perfluorinated methane, ethane, cyclobutane, cyclohexane, methylcyclohexane, and benzene were irradiated in a cobalt-60 γ source to a total dose of 1.1×10^{19} ev ml^{-1}. The gases were measured with a McLeod gauge and analyzed by gas chromatography. The yield of hydrogen from pure cyclohexane and *n*-hexane, $G(H_2)_0$, was found to be 5.6 and 5.2, respectively.

The presence of CF_4 and C_2F_6 in concentrations of up to 3 mole % had no effect on $G(H_2)$. However, a very pronounced depression of the hydrogen yield was observed in the presence of even very low concentrations of perfluorocyclocarbons. The effect of all the cyclic solutes on $G(H_2)$ was found to be almost identical in the concentration range studied (0–3 mole %). From Figure 1 it can be seen that at low concentrations of solutes perfluorocyclobutane appears to have a similar effect in reducing the hydrogen yield as CCl_4. The effects of all the solutes were found to be similar in both solvents. Hydrogen atom scavenging by the solutes would not seem to be plausible as an explanation for the decrease in $G(H_2)$ in the presence of perfluorinated additives. CF_4 is known to be inert toward hydrogen atoms[7] and the C–F bond strength in the cyclic compounds would appear to be higher than that of CF_4. As an example C–F bond dissociation energy for CF_4 and C_4F_8 (cyclic) are 122[8] and 152[9] kcal, respectively. The drop in $G(H_2)$ could not arise from charge transfer from solvent to solute, the ionization potential of perfluorinated compounds being considerably higher than those of hydrocarbons. Electronic excitation transfer in radiolytical paraffinic condensed phase systems would not seem to be an important process.[3d] In the gas phase radiolysis of Xe–C_2F_6 mixtures it was suggested that excitation transfer from Xe to C_2F_6 occurs.[10] However, no decrease in $G(H_2)$ was found in the presence of C_2F_6. In order to confirm our assumption that electron scavenging by perfluorocyclocarbon solutes is responsible for the decrease in $G(H_2)$, solutions of *n*-hexane and cyclohexane containing both N_2O and the perfluorinated compounds were irradiated. Nitrous oxide has been shown to react with electrons produced in irradiated cyclohexane, this reaction resulting in the formation of nitrogen.[11] A second solute competing with N_2O for electrons would thus decrease $G(N_2)$, the relative reactivity $K_{N_2O} = K_{e^-+S}/K_{e^-+N_2O}$ being given by the expression

$$K_{N_2O} = \frac{\Delta G(N_2)[N_2O]}{G(N_2)[S]} \qquad (1)^{12}$$

The results of the competitive experiments are shown in Table I. CF_4 and C_2F_6 had no effect on $G(N_2)$; the perfluorocyclocarbons depressed considerably the nitrogen yield. Calculated K_{N_2O} values are close to unity for all these solutes. The fact that CF_4 does not compete with N_2O for thermal electrons is consistent with the finding that no negative ions have been found upon subjecting CF_4 to bombardment by low-energy electrons.[13] Conclusive evidence is available for the existence of a highly efficient nondissociative thermal electron attachment to perfluoromethylcyclohexane,[14] and

Table I. γ Radiolysis of *n*-Hexane Solutions

Solute, m*M*		Nitrous oxide, m*M*	$G(H_2)^a$	$G(N_2)^a$	$K_{N_2O}{}^b$
		5	4.1	1.18	....
C_4F_8 (cyclic)	3.3	5	4.1	0.73	0.88
C_4F_8 (cyclic)	8.0	5	3.9	0.46	0.98
C_6F_6	3.8	5	3.9	0.71	0.90
C_6F_6	7.7	5	3.7	0.50	0.85
C_6F_{12} (cyclic)	3.2	5	4.0	0.75	0.89
C_6F_{12} (cyclic)	6.4	5	3.8	0.53	0.96
$C_6F_{11}CF_3$	3.5	5	3.9	0.71	0.94
$C_6F_{11}CF_3$	8.0	5	3.7	0.45	1.02

[a] Total dose 1.1×10^{19} ev ml^{-1}. [b] Calculated from eq 1.

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(5) A. A. Altshuler and C. A. Clemons, *Anal. Chem.*, **38**, 133 (1966).

(6) C. N. Works and E. W. Lindsay, *Trans. Am. Inst. Elect. Engin.*, [III] 77, 1659 (1958).

(7) J. R. Dacey and J. W. Hodgkins, *Can. J. Res.*, **B28**, 173 (1950).

(8) C. R. Patrick, *Advan. Fluorine Chem.*, 2, 17 (1961).

(9) M. M. Bibby and G. Carter, *Trans. Faraday Soc.*, **59**, 2455 (1963).

(10) L. Kevan, *J. Chem. Phys.*, **44**, 683 (1966).

(11) (a) G. Scholes and M. Simic, *Nature*, **202**, 895 (1964); (b) G. Scholes, M. Simic, G. E. Adams, J. W. Boag, and B. D. Michael, *ibid.*, **204**, 1187 (1964).

(12) W. V. Sherman, *J. Chem. Soc.*, Sect. A, 599 (1966).

(13) V. M. Hickam and D. Berg, *J. Chem. Phys.*, **29**, 517 (1958).

(14) (a) B. H. Mahan and C. E. Young, *J. Chem. Phys.*, **44**, 2192 (1966); (b) R. K. Assundi and J. D. Craggs, *Proc. Phys. Soc.* (London), **83**, 611 (1964).

the lifetime of the $C_6F_{14}^-$ ion, under collision-free conditions, is at least 1 μsec.

The results presented here would thus strongly suggest the decrease in radiolytical hydrogen yield in the solution of cyclic perfluorocarbons in alkanes is due to electron scavenging by these solutes. The subsequent neutralization reaction between the solvent positive ion and the solute anion would be expected to result in smaller yields of radiolytical products.[15] The main difference between the electron-scavenging abiltiy of the perfluorocyclocarbons and the alkyl and benzyl halogenated compounds would thus lie in the fact that in the case of the former electron attachment is nondissociative, whereas in the latter electron capture has been observed only in the cases where the electron affinity of the halogen atom exceeds the bond dissociation energy of the carbon–halogen bond[2,3,16] and conditions are favorable for the occurrence of a dissociative process. The nondissociative electron attachment of the perfluoro compounds results from the fact that the C–F bond strength exceeds the electron affinity of the fluorine atom. In their ability to accommodate an external electron, the perfluorocyclic compounds would thus seem to be comparable to polynuclear aromatic molecules, several of which, such as naphthalene, naphthacene, pyrene, etc., are known to attach thermal electrons in the gas phase.[17] The comparison of the K_{N_2O} values obtained for anthracene and pyrene, 0.6 and 0.5, respectively,[12] with those obtained for perfluorocyclocarbons would suggest a higher stability of the perfluorinated anions.

(15) P. R. Geissler and J. E. Willard, *J. Am. Chem. Soc.*, **84**, 4627 (1962).

(16) R. F. C. Claridge and J. E. Willard, *ibid.*, 87, 4992 (1965).

(17) W. E. Wenthworth, E. Chen, and J. E. Lovelock, *J. Phys. Chem.*, 70, 445 (1966).

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The Reactions of Selenium Atoms. I. Addition and Insertion Reactions of Selenium (4^1D_2) Atoms with Olefins and Paraffins

Sir:

Reactions of selenium atoms with olefins have been reported by Callear and Tyerman.[1] In flash-photolyzed CSe–olefin mixtures, transient spectra were observed and tentatively assigned to episelenides. From the time dependence of the spectral intensities it was possible to obtain absolute rate constants for a series of olefins. Preliminary experiments were also performed with COSe, and it was concluded that selenium atoms in the 4^1D_2 state were formed by photolysis of COSe in analogy with COS.[2]

Recently in this laboratory a mass spectrometric technique has been developed[3] for the time-resolved detection of transient intermediates in flash-photolyzed systems. Detection does not depend on the electronic absorption characteristic of the transient, and, in combination with kinetic absorption spectroscopy, the technique assumes great flexibility.

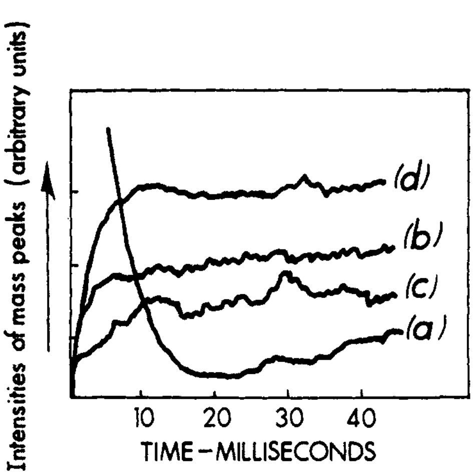

Figure 1. Variation with time of intensities of mass peaks, from oscillograms: (a) decay of Se_2 (*m/e* 160) (full scale 2 v); (b) formation of propyl selenomercaptan (*m/e* 124) (full scale 500 mv); (c) formation of HSe (*m/e* 81) as a fragment of propyl selenomercaptan (full scale 200 mv); (d) formation of an adduct in flashed C_2D_4–COSe with *m/e* 112 (full scale 1 v).

Our apparatus consists, in essence, of a photolysis cell attached to a small leak into the ion source of an Atlas CH_4 mass spectrometer. Selected mass peaks can be studied with a response time of a few milliseconds, and thereafter at times limited by bleeding of the photolyzed mixture into the ion chamber. Typical photolytic flash energies were ~2000 joules, passed into a reaction volume of ~5 ml. A full description of the equipment will appear elsewhere.[3]

Three aspects of selenium atom chemistry were explored: polymerization, insertion into C–H and C–D bonds of paraffins, and addition to olefinic double bonds. Reaction mixtures contained 20 μ of COSe and 300 μ of other reagents and 15 torr of He. Approximately 10% of the COSe was decomposed per flash.

Figure 1(a) shows the rapid production and decay of Se_2 (*m/e* 160); the apparent increase at longer delays is ascribed to the cracking patterns of higher polymers. When ~3 torr of CO_2 was present in the reaction mixture, the Se_2 yield was much decreased, indicating that (like $S(3^1D_2)$) $Se(4^1D_2)$ is deactivated by CO_2 and that the abstraction

$$Se(4^1D_2) + COSe \longrightarrow CO + Se_2 \qquad (1)$$

is more rapid than the analogous reaction of $Se(4^3P)$. Se_3 was not detected in COSe–He mixtures after flashing, which is further indication that the atoms are rapidly consumed by (1).

Experiments with propane, cyclopropane, cyclobutane, ethane, methylsilane, isobutane, etc., demonstrated insertion of excited selenium atoms into C–H and possibly Si–H bonds. Figures 1(b) and 1(c) show formation of propyl selenomercaptan (*m/e* 124) and the corresponding fragment, HSe^{80} (*m/e* 81). For the first three hydrocarbons cited above, the HSe peak was about 10% as intense as those of the parent adducts, indicating that selenomercaptans are major products. Se_2 formation was not suppressed, even though 15-fold excesses of the hydrocarbons were present, showing either that insertion is less rapid than (1), or that

(1) A. B. Callear and W. J. R. Tyerman, *Proc. Chem. Soc.*, 296 (1964); *Trans Faraday Soc.*, **61**, 2395 (1965); *ibid.*, **62**, 371 (1966).

(2) I. G. Csizmadia, K. S. Sidhu, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **88**, 2412 (1966).

(3) W. K. Duholke, R. Messmer, P. Kebarle, O. P. Strausz, and H. E. Gunning, to be published.