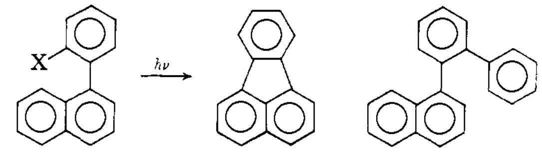
Photolytic Rearrangement and Halogen-Dependent Photocyclization of Halophenylnaphthalenes

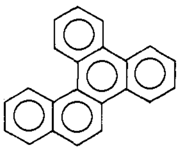
Sir:

The photolysis of halobenzenes in benzene results in homolytic cleavage to give phenyl radicals, which attack the solvent to give biphenyls as well as reduction products.[1,2]

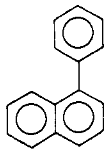
We have attempted an intramolecular analog of this reaction, photocyclization of 1-*o*-halophenylnaphthalenes (I). Surprisingly, on irradiation in deoxygenated benzene with 3130-Å light, the iodo compound I (X = I) decomposed relatively rapidly ($\phi = 5 \times 10^{-2}$) but afforded little or no fluoranthene (II), while the chloro compound I (X = Cl) decomposed only slowly ($\phi = 6 \times 10^{-4}$) but gave fluoranthene as the major product (see Table I). The bromo compound I (X = Br) ($\phi = 1 \times 10^{-2}$) exhibited intermediate behavior.



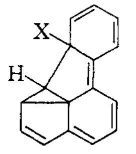
I, X = Cl, Br, I II IV



V



VI



VIII

The other products found by glpc analysis and identified by comparison with authentic samples were 1-phenylnaphthalene (III), 2-α-naphthylbiphenyl (IV), and benzo[*g*]chrysene (V). In separate experiments, it was shown that IV is photocyclodehydrogenated[3] to V, but III does not give fluoranthene II on irradiation.

Table I. Products Formed on Irradiation of *o*-Halophenylnaphthalenes

	Yield, %		
Halogen	II	III	IV + V
Cl	44–59	17–28	24–31
Br	5–8	46–58	37–46
I	0–1	8–15	85–92

The triplet of the iodo compound ($E_t = 60$ kcal)[4] is probably an intermediate in its reactions since sensitization with benzophenone ($E_t = 69$ kcal) affords the same products as direct excitation and with only slightly decreased quantum yield ($\phi = 3 \times 10^{-2}$). The failure of the bromo and chloro compounds (both $E_t = 60$ kcal) to afford products on sensitization and the lower quantum yields on direct excitation imply reaction *via* the singlet and reflect the greater strength of the carbon–bromine and carbon–chlorine bonds.

The intermediacy of the radical VI in the photolysis of the iodo compound I is indicated by the nature of the products. It is also suggested by the finding that the same products are obtained on abstraction of iodine from I (X = I) by thermally generated phenyl radicals.[5]

The radical VI is further implicated by the finding that, at low conversions, the iodo compound I gives a small glpc peak corresponding to 1-iodo-8-phenylnaphthalene (VII). Irradiation of VII, synthesized independently, converts it rapidly to I (X = I) and hence to the photoreaction products of I (X = I). This we believe demonstrates the formation of radicals from I (X = I) and VII, the rapid *photochemical intramolecular interconversion* of the radicals, and ultimate collapse to the parent compounds. These isomerizations have some analogy in the work of DeTar and Reylea,[6] who found that the radical generated from the diazonium salt of 2-amino-4′-methylbenzophenone underwent intramolecular hydrogen transfer.

The great influence of the halogen on the ratio of intramolecular to intermolecular reaction, as shown in Table I, could be explained by the differences in lifetimes of the excited singlets produced on irradiation. Because of the heavy atom effect, the singlet of the chloro compound has a longer lifetime than that of the iodo compound, and therefore might have time to form a cyclic intermediate of the type VIII,[7] which could eliminate hydrogen halide to give fluoranthene. The failure to observe photocyclodehydrogenation of III in the presence of oxidants argues against this explanation, although it may not serve as a proof since *photocyclodehydrohalogenations* are known to occur more efficiently.[8]

Molecular orbital calculations indicate that disrotatory ring closure to *cis*-VIII is permitted both thermally and photochemically.[9] Experimentally, no thermal formation of fluoranthene from the iodo or bromo compounds could be detected.

An alternative explanation for the change in yield of fluoranthene involves the difference in electronegativity of the halogens. The halogen radical formed on irradiation of I remains in the solvent cage (and often recombines with the aryl radical[10]). The much greater electron affinity of the chlorine atom[11] may then impart more carbonium ion character to the aryl radical, through a charge-transfer interaction or possibly through a simple redox reaction.[12] By analogy with the work of DeTar and Chu,[13] the greater carbonium ion

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[1] W. Wolf and N. Kharasch, *J. Org. Chem.*, **26**, 284 (1961); 30, 2493 (1965).

[2] T. Matsuura and K. Omura, *Bull. Chem. Soc. Japan*, **39**, 944 (1966); N. Kharasch, R. K. Sharma, and H. B. Lewis, *Chem. Commun.*, 418 (1966).

[3] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964).

[4] Triplet energies determined from phosphorescence spectra in a 3-methylpentane glass.

[5] Iodine atom abstraction from iodobenzene by phenyl radicals thermally generated from dibenzoyl peroxide has been demonstrated by J. F. Bunnett and C. C. Wamser, *J. Am. Chem. Soc.*, **88**, 5534 (1966).

[6] When the radical was generated in carbon tetrachloride, 2-chloro-4-methylbenzophenone as well as 2-chloro-4′-methylbenzophenone was isolated: D. I. Reylea and D. F. DeTar, *ibid.*, **76**, 1202 (1954); D. F. DeTar and D. I. Reylea, *ibid.*, **78**, 4302 (1956).

[7] Six bicyclo[3.1.0]hexane-containing structures of this type can be written as possible intermediates.

[8] S. M. Kupchan and H. C. Wormser, *Tetrahedron Letters*, 359 (1965); B. S. Thyagarajan, N. Kharasch, H. B. Lewis, and W. Wolf, *Chem. Commun.*, 614 (1967).

[9] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

[10] W. Wolf and N. Kharasch,[1] using iodine-131, have demonstrated the photochemical reversibility of radical formation from 2-iodobiphenyl.

[11] G. Briegleb, "Electronen Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961, p 183.

[12] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 33.

[13] D. F. DeTar and C. Chu, *J. Am. Chem. Soc.*, **82**, 4969 (1960), found the carbonium ion generated from the diazonium salt of 2-aminobenzophenone gave mostly fluorenone while the radical in benzene gave 2-phenylbenzophenone and only a trace of fluorenone.

character would in turn be expected to enhance the rate of intramolecular reaction to give fluoranthene.

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Radiolysis of Nitrous Oxide in the Adsorbed State[1]

Sir:

The radiolysis of molecules physically adsorbed on solids often results in such large decomposition compared to that in the liquid and gaseous states that energy directly absorbed by the solid must be transferred to the sorbate.[2-7] This apparent energy-transfer phenomenon is incompletely understood at present. Nitrous oxide is a well-known electron scavenger, and one of its decomposition products, nitrogen, is unlikely to chemisorb on the sorbent surface. Results on the radiolysis of N_2O adsorbed on silica gel[8] at 10° are reported here. Experimental methods have been described elsewhere.[9]

Experiments in which N_2O adsorbed on unirradiated and irradiated sorbent (dose, 40×10^6 rads) resulted in negligible N_2O decomposition compared to that when sorbent and N_2O were irradiated together. The products measured were N_2 and O_2, and in three series of experiments in which dose, surface N_2O concentration, and surface hydroxyl concentration were varied, the nitrogen to oxygen ratios found were 2.0 ± 0.1, 2.3 ± 0.3, and 1.9 ± 0.1. The stoichiometry of the decomposition is apparently

$$N_2O \longrightarrow N_2 + 0.5O_2$$

In all experiments, 97 ± 2% of the nitrogen desorbed at room temperature while, depending on the experiment, some 50–90% of the total amount of oxygen was observed. The remaining oxygen could only be recovered by degassing at 450° and was apparently chemisorbed on the surface. The greater the total amount of oxygen the smaller was the fraction retained on the surface at room temperature. No hydrogen was detected in the radiolysis products.

At constant surface coverage or electron fraction of N_2O, $G(N_2)$ was independent of dose up to 25 Mrads but decreased with further increase in dose. At a constant dose of 19 Mrads, $G(N_2)$ increased with electron fraction and appeared to be approaching a constant value at about 0.05 electron fraction (Figure 1). The $G(N_2)$ values observed (0.52 at electron fraction 0.0004 to 3.1 at 0.05) are so high that efficient energy transfer from the solid to the adsorbed N_2O must be taking place.

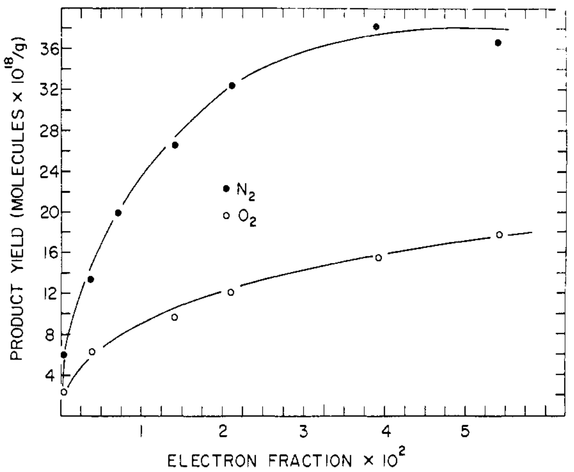

Figure 1. Formation of N_2 and O_2 as a function of electron fraction of N_2O adsorbed on silica gel (dose, 19×10^6 rads).

The results in Figure 1 can be explained by invoking electrons as energy-transfer carriers. Electrons formed in the bulk solid migrate rapidly to the surface where they either react with N_2O or become trapped. The O^- and trapped electrons then react with the positive holes (+) (eq 1–4). Volume trapping of electrons or positive holes in the bulk sorbent is considered to be negligible, since for this particular gel they will always be within 11 Å of the surface.

$$e^- + (N_2O)_S \longrightarrow N_2 + (O^-)_S \quad (1)$$

$$e^- + \text{surface} \longrightarrow (e^-)_S \quad (2)$$

$$\oplus + (e^-)_S \longrightarrow \text{energy} \quad (3)$$

$$\oplus + (O^-)_S \longrightarrow (O)_S \quad (4)$$

This mechanism leads to the relationship

$$G(N_2) = \frac{G_{e^-}k_1\theta}{k_1\theta + k_2(1 - \theta)} \quad (5)$$

where θ = surface coverage of N_2O = $(v)_S/v_m$ = (amount of N_2O sorbed)/(amount of N_2O at monolayer coverage). Rearrangement of eq 5 gives

$$\frac{k_1 - k_2}{k_1G_{e^-}} + \frac{k_2v_m}{k_1G_{e^-}(v_{N_2O})_S} = \frac{1}{G(N_2)} \quad (6)$$

and a plot of $1/G(N_2)$ *vs.* $1/(v_{N_2O})_S$ or $1/N_2$ *vs.* $1/(v_{N_2O})_S$ should be linear as is found in Figure 2 in the range θ = 0.01–0.20. From the slope and intercept and taking 17 Å^2 for the area of the N_2O molecule, $G_{e^-} = 3.7$ and $k_2/k_1 = 2.9 \times 10^{-2}$.

If the electrons are assumed to be first trapped on the surface, before reacting with N_2O or positive holes, eq 7, similar to eq 6, results, where $k_2' = k_1[\oplus]$, and concentrations are expressed per unit area of solid.

$$\frac{1}{G_{e^-}} + \frac{1}{G_{e^-}}\frac{k_2'}{k_1(N_2O)_S} = \frac{1}{G(N_2)} \quad (7)$$

G_{e^-} is then 3.9 and k_2'/k_1 = 215 µmoles/g = 0.28 µmole/m^2. This mechanism predicts that $G(N_2)$ is dependent on dose rate. In preliminary experiments $G(N_2)$ has

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] (a) J. M. Caffrey, Jr., and A. O. Allen, *J. Phys. Chem.*, **62**, 33 (1958); (b) J. W. Sutherland and A. O. Allen, Proceedings of the Conference on Large Radiation Sources in Industry, IAEA, 1960; *J. Am. Chem. Soc.*, **83**, 1040 (1961).

[3] R. Coeklebergs, A. Crucq, and A. Frennet, *Advan. Catalysis*, **13**, 55 (1962).

[4] J. G. Rabe, R. Rabe, and A. O. Allen, *J. Am. Chem. Soc.*, **86**, 3887 (1964); *J. Phys. Chem.*, 70, 1098 (1966).

[5] R. R. Hentz, *ibid.*, **65**, 1470 (1961); **66**, 1625, 2714 (1962); **68**, 2889 (1964).

[6] A. V. Topchiev, Yu. A. Kolbanovsky, L. S. Polak, Yu. L. Khait, and E. B. Shilkter, *Neftekhimiya*, **1**, 105 (1961).

[7] G. M. Zhabrova, V. B. Kazanskii, V. I. Vladimirova, B. M. Kadenatsi, and G. B. Pariiskii, *ibid.*, **4**, 753 (1964).

[8] Davison silica gel, grade 40. Surface area, 760 m^2/2; pore volume, 0.43 cc/g; average pore diameter, 22 Å.

[9] J. W. Sutherland, D. Sethi, and R. Goodrich, *J. Phys. Chem.*, **71**, 4422 (1967).