

temperature which depends both on explosion energy and pressure.

The conservation equation

$$p_1 - p_0 = \rho_0 (1 - \rho_0/\rho_1) D^2 \quad (2)$$

combined with equation (1a) gives, when $p_0 \ll p_1$, p_1 is expressed in kbar, ρ in g/cm³ and D in km/s

$$p_1 = 10 \rho_0 \frac{0.140 + 0.260 \rho_0}{0.140 + 1.260 \rho_0} D^2 \quad (3)$$

In the range $0.8 < \rho_0 < 1.8$ g/cm³, equation (3) can be written

$$p_1 = 2.1 (0.36 + \rho_0) D^2 \quad (4)$$

Using Mader's values for D in equation (3) we get the values of p_1 as a function of ρ_0^2 which are shown in Fig. 1. The values show that for each explosive p_1 is approximately proportional to ρ_0^2 in the important range $1.0 < \rho_0 < 1.6$ g/cm³, that is

$$p_1 = a \rho_0^2 \quad (5)$$

The proportionality constant a has a value of 75 kbar/(g/cm³)² for TNT, 85 for tetryl and picric acid, 99 for PETN and 103 for RDX and HMX.

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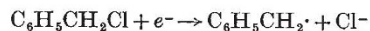
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Free Radicals in the Radiolysis of Benzyl Halides

ULTRA-VIOLET absorption spectroscopy can be used to study the production of radicals by photolysis or radiolysis if solutions in rigid media, such as *MP* (2 parts methyl-cyclohexane, 3 parts isopentane) at 77° K, are used. The photolysis of toluene, benzyl chloride and similar compounds, to give benzyl and related radicals, has been studied in detail¹. It was soon realized² that γ -radiolysis gave spectra different from those given by ultra-violet photolysis and this was later confirmed by spectrographic study of the series—C₆H₅CH₃, C₆H₅CH₂Cl, C₆H₅CHCl₂, C₆H₅CCl₃ (ref. 3). The results seemed to show that γ -radiolysis led to breaking of the α -C—H bond while photolysis broke the C—Cl bond. Gallivan and Hamill⁴, however, have found strong evidence that the dominant process in the radiolysis of these halides is dissociative electron attachment; for example



A positive ion of the solvent is also trapped. They observed the same spectral differences and therefore suggested that the spectrum is that of the benzyl radical perturbed by the neighbouring chloride ion which does not escape from the solvent cage. Surprisingly, chloride, bromide and iodide gave identical spectra, but it may be that the nature of the anion is not important.

We report here some new observations of this system. The preparation of samples and experimental method have already been described³; once again, after γ -radiolysis at 77° K, the four compounds gave absorption peaks at 3175, 3200, 3250 and 3240 Å respectively. If the samples were warmed to 90° K for a few minutes and then re-cooled, peaks were observed at 3175, 3175, 3210 and 3240 Å respectively, that is, marked shifts had occurred in two cases; longer periods of warming caused the spectra

to disappear. Two explanations of this effect appear plausible: for benzyl chloride, either (a) C₆H₅CHCl· is first formed and is replaced by C₆H₅CH₂· or (b) C₆H₅CH₂·, Cl⁻ is first formed and the Cl⁻ escapes from the solvent cage on warming. The solvent cation will probably be trapped close to the anion in these non-polar glasses so that the recombination of the ions may cause further complicated reactions involving the benzyl radicals. Explanation (b) appears to be the more plausible and we will assume it to be correct, but the lack of shift in the case of benzotrichloride is surprising.

The problem is being investigated further by making quantitative absorption measurements with a Cary Model 14 spectrophotometer. Absolute wavelength measurements may be less accurate than in the photographic work³ but the values are likely to be reproducible within a few angstroms. Samples are irradiated at 77° K and changes in the spectra are followed isothermally at 87° K (liquid argon) or 90° K (liquid oxygen). To slow down the radical diffusion processes harder glasses are used (for example, 2 parts methylcyclohexane, 1 part isopentane).

Peaks have been observed initially at 3200 (C₆H₅CH₂Cl), 3242 (C₆H₅CHCl₂), and 3200 Å (C₆H₅CH₂Br). On warming, the peaks broaden and, over a period of a few minutes, sharpen again at the new position with an optical density reduced by a factor of between 2 and 4. The new spectra then decay slowly over a period of several hours. The marked difference in the rates of the two processes is consistent with explanation (b); first-order separation of ion and radical will be much faster than second-order reactions which remove the radicals. The initial rapid loss of radicals may be caused by a reaction with neighbouring solvent radicals (or cations) which is effectively first order.

When solutions of C₆H₅CH₂Br were warmed, the new peak appeared at 3175 Å; this was also produced by benzyl chloride in these experiments and previously^{1,3} by the photolysis of toluene; it can be confidently identified with the benzyl radical. C₆H₅CHCl₂ gives a peak at 3222 Å which is presumably attributable to C₆H₅CHCl·. This wavelength differs significantly from that of the peak first obtained from C₆H₅CH₂Cl; this lends further support to explanation (b). Subsequent recooling to 77° K had no effect on any of the spectra.

The behaviour of benzyl chloride is more complicated: on warming, the 3200 Å band is replaced by two peaks at 3175 and 3215 Å, the order in which they appear depending on the viscosity of the solvent. The band at 3175 Å decays more rapidly and after several hours the spectrum closely resembles that of C₆H₅CHCl, but the small shift in wavelength (7 Å) may be significant; it appears that both benzyl and a second radical are produced on warming. Attack on the solute by benzyl or solute radicals or reaction with neighbouring solvent cations may be involved.

We thank the Science Research Council for a grant for the purchase of the Cary spectrophotometer and one of us (M. I. S.) thanks the Commonwealth Scholarship Commission, U.K., for a scholarship and Karnatak University, Dharwar, for study leave.

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Received October 28, 1966.

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