ters are energy degenerate. The GO's embracing the skeleton and those of the C^- system are symmetrically disposed energy-wise with respect to the group theoretic species (in D_{3h} only) and energy. Interaction will then be to a first approximation also symmetric.

Efforts were made to take account of the inductive effect due to the difference in field of NO_2 as compared to C^- and of the resonance effect due to the π-orbital extension. Constants involved were evaluated from a *postulated* spectroscopic assignment of the electronic transitions of TNB and an ionization potential. This assignment was itself tenuous, and the value of 1.1 e.v. for the electron affinity of TNB can be questioned.

The ground configurations of TNB and TNB^- are believed accurately given by

$$\ldots\ldots (a''_2)^2\,(e'')^4\,(a''_2)^2\,(e'')^4,\ {}^1A_1 \text{ and}$$

$$\ldots\ldots (a''_2)^2\,(e'')^4\,(a''_2)^2\,(e'')^4\,(e'')^1,\ {}^2E'',$$

respectively.

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The Role of Hydrogen Iodide in the Photoisomerization of n-Propyl Iodide[1]

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Air-free and air-saturated samples of liquid n-propyl iodide have been photolyzed, principally with the 2537 Å. mercury line. Tracer experiments with I^{131} have shown that the isomerization to isopropyl iodide is a slow post-irradiation process and is inhibited if oxygen was present during the photolysis but not if oxygen is admitted after photolysis to a previously air-free sample. The isopropyl iodide is formed from propylene and hydrogen iodide; the presence of the latter intermediate was established by titration. The primary product ratio HI/I_2 is 0.53 at 30° and 0.91 at $-60°$ and increased isomerization at Dry Ice temperature follows the increased production of HI. Interpretation of the results favors a diffusion-controlled reaction. Equations are proposed for the various parts of the reaction and quantum yields calculated for each of the successive and competing steps.

When n-propyl iodide is decomposed by irradiation with ultraviolet light, the main products are iodine, propane, propylene and isopropyl iodide. It has been proposed[2] that the isopropyl group arises not from any free radical rearrangement, but from the combination of propylene with HI, with the assumption that the latter is produced as an intermediate in the photolysis. The experimental evidence supporting this proposal was somewhat indirect, although it was shown that HI results from the photolysis of ethyl iodide[3]; this latter result was confirmed in an extensive study by Bunbury, Williams and Hamill,[4] and these investigators have shown that the experimental results require a radically new interpretation of the mechanism of photolysis of ethyl iodide. Since there are many correlations between photolysis and radiolysis of alkyl iodides, it was natural to suppose that HI might also be a product of radiolysis, and this has been shown to be true.[4,5]

In order to verify fully the original inference and explore the implications in a more complex system it seemed desirable to demonstrate the presence of HI in photolyzed n-propyl iodide in a direct manner. In this connection it was also of interest to examine more carefully the effects on the photoisomerization due to change of wave length, temperature or presence of dissolved air in the material being photolyzed.

Experimental

Purification of Alkyl Iodides.—Five hundred gram batches of Matheson iodides were washed with aqueous thiosulfate, dried and distilled at 100 mm. pressure through a six-foot column packed with glass helices. The central fifth was used for photolysis and the second and fourth fifths, or a little more, were used for carriers.

Apparatus.—The mercury lamp was similar to one described previously.[2] However, in order to maximize the 1849 Å. contribution, the lamp helix was specially fabricated from very thin quartz tubing (wall thickness <0.6 mm.).

The cells used for photolysis were 13 × 200 mm. cylinders of thin quartz (wall thickness 0.6 mm.) for transmission of the 1849 Å. radiation, and similar cylindrical cells of 1.0 mm. Vycor (Corning 7910 glass) which has a cutoff at *ca.* 2400 Å. The cells were provided with a quartz-to-Pyrex graded seal for attachment to the vacuum line, and also with a side arm sealed with a break-off through which carriers and other materials could be introduced into the cell after photolysis.

Procedure for Photolysis.—Five-ml. or 10-ml. samples of n-propyl iodide, frequently containing dissolved elemental I^{131}, were dried and degassed on the vacuum line as previously described.[2] For some runs when radioiodine was not used, the sample was merely deaerated by bubbling dry nitrogen or hydrogen through it for 30 minutes and the cell then sealed by a glass joint lightly smeared with silicone grease. The cell, with vapor space screened with black tape, was placed in the center of the lamp helix, and the temperature kept approximately constant at 32 ± 5° by blowing a stream of air through the lamp assembly. For the low temperature runs, the cell and sample were chilled in a Dry Ice–acetone mixture, wiped quickly, irradiated for two minutes, chilled for one minute and the cycle continued. Dummy runs indicated that the temperature of the absorbing layer was *ca.* $-60 \pm 15°$ during the irradiations.

Analysis of Samples Containing I^{131}.—After photolysis the sealed cell was stored in the dark for periods ranging from 5 minutes to 30 hours, and the contents were then added to a carrier mixture of iodides and inert I_2. A 5-ml. aliquot of this mixture was diluted to 50 ml. with CCl_4 and its total and organic activity measured in an annular-jacketed GM tube as described elsewhere.[6] The remaining

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[1] Presented at the 131st meeting of the American Chemical Society, Miami, Florida, April, 1957.

[2] C. E. McCauley, W. H. Hamill and R. R. Williams, Jr., THIS JOURNAL, **76**, 6263 (1954).

[3] This possibility had been suggested much earlier by G. Emschwiller, *Compt. rend.*, **192**, 799 (1931), but seems to have passed unnoticed.

[4] D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **78**, 6228 (1956).

[5] (a) E. O. Hornig and J. E. Willard, *ibid.*, **79**, 2429 (1957); (b) R. J. Hanrahan and J. E. Willard, *ibid.*, **79**, 2434 (1957).

[6] C. E. McCauley, G. J. Hilsdorf, R. J. Geissler and R. H. Schuler, *ibid.*, **78**, 3246 (1956).

carrier mixture was washed with thiosulfate, dried, fractionated and 5-ml. cuts of the propyl iodides diluted to 50 ml. with CCl_4 and counted as before.

Addition of Oxygen to a Deaerated System after Photolysis.—To test the effect of oxygen on post-irradiation isomerization, the sample cell was fitted with a side arm ending in a fine sealed capillary tube. After photolysis the capillary tip was broken in a balloon filled with dry air and then resealed in a small flame and the cell shaken vigorously for 15 minutes to aerate the liquid. The vapor space in the cell was sufficiently large that even after saturation the pressure was essentially atmospheric. The cell was then stored in the dark for 20–30 hours, then analyzed as above.

Analysis for I_2 and HI in Non-radioactive Runs.—For these experiments the photolysis cell was fitted with a side arm holding a Pyrex cuvette. The latter could be filled by merely tipping the cell and the absorption due to the I_2 measured at 600 or 650 mμ in a Beckmann DU spectrophotometer. The cell was then opened and the contents extracted with distilled water. The HI was determined by titrating an aliquot of the extract with 0.01 *N* base, using methyl red as indicator. Preliminary experiments showed that no detectible amount of I_2 was extracted from the alkyl iodide into the water phase.

Results

Linearity of Iodine Production with Dose.—Since it is known[7,8] that the iodine–alkyl iodide complex $RI \cdot I_2$ has a very high extinction coefficient at 2537 Å., it was desirable to determine whether any falling off of iodine production occurred under the high dosages ($2\text{–}5 \times 10^{19}$ quanta/ml.) used in these experiments. Duplicate runs showed that the iodine production in the photolysis of air-free *n*-propyl iodide is linear with dose even for total irradiations much greater than those used in this investigation.

Results of Tracer Experiments.—Table I summarizes the distribution of organic radioiodine resulting from the photolysis of air-free *n*-propyl iodide in the presence of small amounts of elemental I^{131}. Since earlier work[2] had shown that no ethyl iodide was produced and only trace amounts of methyl iodide, these two materials were not included in the carrier mixture. Percentages were calculated from the sum of activities of the *n*-propyl and isopropyl iodide fractions and the excess activity in the stillpot residue, each properly weighted for volume of carrier. Comparison of this sum with the original unfractionated organic mixture showed the material balance to be quite good.

TABLE I

DISTRIBUTION OF ORGANIC I^{131} AFTER PHOTOLYSIS

Sample air-free; $T = 32 \pm 5°$; initial I_2 concn., *ca.* 3×10^{-3} *M*.

Storage after irradiation, hr.	% isoPrI[a]	% *n*-PrI[a]	Cell
10 min.	3.5	96.2	Quartz
15 min.	5.4	94.2	Quartz
1.5	11.1	88.4	Quartz
10	28.4	71.5	Quartz
17	26.2	73.3	Vycor
20	29.6	70.3	Quartz
20	32.8	66.3	Vycor
25	29.9	70.1	Quartz
25	33.0	66.2	Vycor
30	31.9	67.7	Quartz
30	31.1	66.6	Vycor

[a] Excess activity in residue accounts for difference between sum of organic activities and 100%.

Two blank runs which included the usual preparation, degassing, storage, workup, but no irradiation, showed organic retentions of 0.3 and 0.4%, respectively, instead of the 35–50% found in irradiation runs. For the second of the two blank runs a sample was used which contained a considerable amount of dissolved propylene. It is clear that the procedure does not produce any significant amount of fictitious organic activity.

Two air-saturated samples were photolyzed and worked up as usual after 20–30 hours storage. Only 3.1 and 2.7% of the organically bound radioiodine appeared as isopropyl iodide, in contrast to the *ca.* 32% indicated for air-free samples in Table I. When air was admitted immediately after photolysis of air-free samples, the percentages of isopropyl activity were 24.8% (20 hours storage) and 27.3% (28 hours storage). The isomerization is thus significantly inhibited by air only if the latter is present during the actual dissociation of the iodide into radicals, even though the actual formation of isopropyl iodide takes place during the storage period after irradiation. Evidently the principal inhibitor is not oxygen but most probably propylperoxy radicals and propyl hydroperoxide which oxidize the HI.

Measurements of HI and I_2.—In the non-radioactive runs, the iodine produced was determined photometrically and the hydrogen iodide by titration. In order to increase the yield of HI and hence the accuracy of the titration a larger lamp current was used than in the experiments with radioiodine. The average yields were 4.47 μmole of HI and 8.38 μmole of I_2 per ml. of irradiated iodide, giving an HI/I_2 ratio of 0.53. The yields of HI are those actually measured, with no correction for the fraction (probably 5–10%) of the original yield which had combined with propylene during the photolysis and the measurement of I_2. No appreciable difference was found between samples deaerated by bubbling in dry H_2 or N_2 and those subjected to the more laborious degassing on the vacuum line.

When air is present in the sample during photolysis, the yield of HI found immediately after irradiation is much less than half of the normal yield; when the sample is saturated with oxygen at 760 mm., only a negligibly small yield of HI is found; correspondingly, the yield of I_2 is increased. Evidently the oxidation of HI by propylperoxy radicals and probably also by propyl hydroperoxide is much more rapid than the addition of HI to propylene.

Photolyses at Low Temperature.—Samples of *n*-propyl iodide containing dissolved I^{131}, when photolyzed at $-60°$ and stored for 20 hours, showed an average of 59.3% of the organically bound radioiodine in the isopropyl iodide fraction. This contrasts with the *ca.* 30% shown in Table I. With the same time of illumination and lamp current that were used in the room temperature photolyses, runs at $-60°$ yielded 6.29 μmoles of HI and 5.74 μmoles of I_2 per ml. of irradiated sample. The absolute yield of HI is evidently much greater than at room temperature and the ratio $HI/I_2 = 0.91$. The total

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(7) E. Cochran, W. H. Hamill and R. R. Williams, Jr., THIS JOURNAL **76**, 2145 (1954).

(8) R. M. Kieffer and L. J. Andrews, *ibid.*, **74**, 1891 (1952).

number of gram-atoms of inorganic iodine formed (I_2 and HI) is seen to be smaller than that found in the experiments at room temperature. This may, however, be partly fictitious since during each low temperature irradiation the cell gradually acquired a light coating of frost which may have scattered some of the incident radiation so that the effective dose was smaller than expected. If this be so, the true yield of hydrogen iodide should be even larger than that shown.

Discussion

The above results seem to offer satisfactory evidence that hydrogen iodide is produced in the photolysis and that the product isopropyl iodide results from the combination of HI and propylene. Apparently even at the high excitation of the photolytic act, the *n*-propyl radicals do not rearrange. Table I, however, does not give any evidence for dependence of HI on wave length. The earlier suggestion[2] that 1849 Å. radiation was much more effective than 2537 Å. in producing HI was due to neglect of the time factor for equation 4 below. This latter is in the present work a "slow" reaction because of the very low concentrations of the reacting species; however, if the reaction is assumed to be bimolecular, an estimate of the rate constant from the second and third measurements of Table I gives $k \cong 0.5$ liters mole^{-1} min.$^{-1}$ which would be considered very fast on a macro-scale. The number has, however, no absolute significance, since the addition is strongly catalyzed by iodine.[9]

Equations for Reaction.—The course of the photolysis seems thus fairly well described by the following equations, which are similar to those proposed for ethyl iodide and presumably will apply to most other alkyl iodides having at least one beta hydrogen.

$$CH_3CH_2CH_2I + h\nu \longrightarrow (CH_3CH_2CH_2 + I) \tag{1}$$

$$CH_3CH_2CH_2I + h\nu \longrightarrow CH_3CH{=}CH_2 + HI \tag{2a}$$

and/or

$$(CH_3CH_2CH_2 + I) \longrightarrow CH_3CH{=}CH_2 + HI \tag{2b}$$

$$CH_3CH_2CH_2 + HI \longrightarrow CH_3CH_2CH_3 + I \tag{3}$$

$$CH_3CH{=}CH_2 + HI \longrightarrow CH_3CHICH_3 \tag{4}$$

$$(CH_3CH_2CH_2 + I) \longrightarrow CH_3CH_2CH_2I \tag{5}$$

$$CH_3CH_2CH_2 + I_2 \longrightarrow CH_3CH_2CH_2I + I \tag{6}$$

$$I + I \longrightarrow I_2$$

Parentheses enclose original dissociation partners which may react after back diffusion. It does not seem necessary to include a reaction similar to 5 but involving fragments from different molecules, since the concentration of iodine atoms in the steady state will presumably always be small compared to I_2 and HI molecules. Equation 3 has been written for the production of propane in place of the previously proposed reaction[2] $CH_3CH_2CH_2 + CH_3CH_2CH_2I \rightarrow CH_3CH_2CH_3 + CH_3CH{=}CH_2 + I$, since it has been shown by experiments with deuterium tracer[4] that the reaction analogous to 3 accounts for most, and possibly all, of the ethane produced from ethyl iodide.

The quantum yields of each of the foregoing reactions may be calculated as follows.[10] $\phi_3 = \phi_{\text{propane}} = \phi I_2 = 0.123$ from Cochran's work.[7] Table III gives the measured I_2/HI ratio as 1.92, but the first entry in Table I shows that about 10% of the original net HI has reacted already. The true ratio I_2/HI ($= \phi_3/\phi_4$) is thus $\cong 1.73$ and

$$\phi_4 = \phi_{\text{orig net HI}} = 0.07, \text{ and}$$

$$\phi_2 = \phi_{\text{orig } C_3H_6} = \phi_{\text{orig HI}} = \phi_3 + \phi_4 = 0.12 + 0.07 = 0.19$$

Under the assumption that equilibria such as $I^{127}I^{131} + HI^{127} \leftrightarrows I_2{}^{127} + HI^{131}$ are attained very rapidly[11] the end data of Table I afford a measure of the ratio of reactions 4 and 6. It is to be noticed, however, that the terminal ratio 32%/68% underestimates the actual production of isopropyl iodide, since slow reaction 4 occurs principally after the original specific activity of the iodine has been diluted by the I_2 produced by photolysis. A rough calculation from the amount of radioiodine taken up by *n*-propyl iodide and the I_2 dilution factor indicates that the figure for isopropyl iodide should be about 45%. With this correction, $\phi_4/\phi_6 = 45/55$ and $\phi_6 = 0.09$. This figure, of course, applies only to propyl iodide samples that initially contained no or very little added iodine. It is interesting to note that in a system where the ratio $I_2/HI = 1.73$ the values $\phi_3 = 0.12$ and $\phi_6 = 0.09$ indicate that reaction 3 is faster than reaction 6. It is uncertain whether this is due to an energy or a steric factor.[12]

The quantum yield of back-reaction 5 depends to a small extent on the mechanism by which HI is

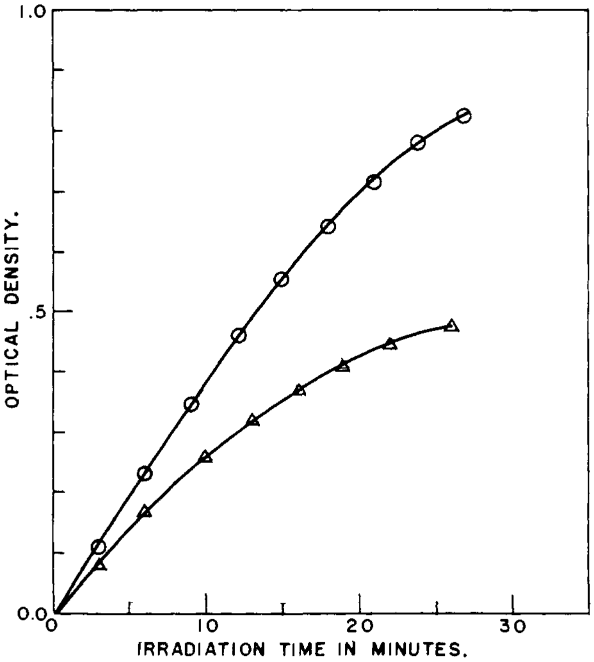

Fig. 1.—Photolysis of *t*-butyl iodide at 32°, I_2 concentration measured at 600 mμ: ○, sample with 4 min. intervals between irradiations; △. sample with 30 min. intervals between irradiations.

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[9] M. S. Kharasch, J. A. Norton and F. R. Mayo, THIS JOURNAL, **62**, 81 (1940).

[10] The HI produced by reaction 2 is referred to as "original HI," some of this disappears immediately by reaction 3. The remainder, which will be used up slowly in reaction 4, is referred to as "original net HI" and is the maximum observable HI.

[11] W. Libby, *J. Chem. Phys.*, **8**, 348 (1940).

[12] R. A. Ogg, Jr., THIS JOURNAL, **56**, 526 (1934).

produced. If $\phi_{2a} = 0$, then $\phi_1 = 1.00 = \phi_{2b} + \phi_3 + \phi_5 + \phi_6$ from which we get $\phi_5 = 0.60$. This happens to be identical with the yield for back-reaction in ethyl iodide calculated by Bunbury, Williams and Hamill from quite different experiments but with the analogous assumption that $\phi_{2a} = 0$.[4]

Linearity of Iodine Production with Time.—It frequently has been observed that ϕ_{I_2} is independent of amount of photolysis in a pure alkyl iodide. The mechanism proposed in equations 1–6 indicates that this observed independence is due to the fact that the measurements of I_2 were completed in a time short enough so that the natural ratio of HI/I_2 had not been decreased significantly by the occurrence of slow reaction 4. It would be predicted, therefore, that if a more reactive olefin than propylene were involved, a gradual decrease of ϕ_{I_2} with extent of photolysis should be observed. To test this prediction, we have photolyzed two samples of *t*-butyl iodide, each for eight three-minute periods, and in the second sample have interposed a 30-minute rest period between successive exposures to the lamp. The results are shown in Fig. 1 and the decrease in ϕ_{I_2} is evident.

Temperature Dependence.—The very large amount of isomerization observed at low temperatures evidently is correlated with the fact that both the absolute yield of HI and the HI/I_2 ratio are much greater at −60° than at room temperature. It also seems probable, but not certain, that ϕ_{I_2} has decreased at −60°.

The mode of formation of HI given in equation 2b will almost certainly be a function of temperature because of "cage effects," and it seems possible to explain both the increase in ϕ_{HI} and the decrease in ϕ_{I_2} in this way. The probability of back-diffusion of two separated radical partners depends strongly on the distance of the initial separation when the latter is small.[13] At low temperatures one expects that the liquid cage walls will be stronger and that the initial separation of iodine atom and propyl radical will be smaller. The probability of back-diffusion of partners should thus be much greater than at room temperature. Under these conditions ϕ_{2b} and ϕ_5 will increase, though possibly to an unequal degree, with consequent diminution of ϕ_{I_2}. The familiar nature of this picture thus gives some support to reaction 2b as the source of hydrogen iodide.

[13] R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950); J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **76**, 3274 (1954).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Kinetics of the Vapor Phase Photochlorination of Trifluorochloroethylene[1]

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The rate of the vapor phase chlorination of $CF_2{=}CFCl$ has been studied at room temperature. There is practically no dark reaction. The rate is independent of olefin pressure in the range of 25 to 400 mm. The rate has been found to depend on the 3/2 power of the chlorine pressure when the latter is low. The rate depends on the square root of the light intensity. The effect of added NO is normal and 10 mm. of this gas will completely stop the reaction. When O_2 at a partial pressure of 8 mm. or more is added to a mixture of a 100 mm. each of Cl_2 and $CF_2{=}CFCl$, an instantaneous reaction takes place at room temperature in a dark room. This reaction is accompanied by the emission of light. Apparently Cl_2 sensitizes the rapid oxidation of $CF_2{=}CFCl$ and very little activation energy is required. At 4 mm. O_2 it appears to inhibit the reaction slightly. A conventional mechanism is offered.

In connection with studies on various chemical and physical properties of fluorocarbons under way in this Laboratory, the kinetics of the photochemical chlorination of trifluorochloroethylene is being studied. The photochemical addition of chlorine to ethylene[2] and the chloroethylenes have been thoroughly studied.[3-11] However, there appear to be no data available on the corresponding reactions of substituted ethylenes containing fluorine. The heat of chlorination of trifluorochloroethylene previously has been determined in this Laboratory.[12] It is 48.8 kcal./mole while the heat of chlorination of ethylene is 43.6 kcal./mole.

Experimental Method

A manometric method was employed to indicate the progress of the reaction. The reaction cell was a Pyrex cylinder 15 cm. long and 3 cm. in diameter. It had optically flat windows and two outlets. One outlet was closed in all runs except those using oxygen. The other was sealed to a stopcock and a number 18/7 ball joint. A small side arm was sealed on just below the stopcock and was used for condensing the reactants by means of liquid nitrogen. The cell, including the side arm, was enclosed in a light tight box which was fitted with optically flat windows. A standard taper joint (10/30 capillary) was attached to the exit line just above the lid of the box. A manometer was connected to this.

Matheson chlorine (purity 99.5%) was taken from a tank, degassed and distilled at Dry Ice temperature into a Pyrex storage bulb. Trifluorochloroethene was furnished through the courtesy of the Kinetics Chemical Division of the du Pont Company. It was scrubbed with 10% KOH solution and a 10% H_2SO_4 solution to remove the inhibitor. After

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[1] This research is being supported by United States Air Force Research and Development Command Contract Number AF 18(600)-1151.

[2] T. D. Stewart and B. Werdenbaum, THIS JOURNAL, **57**, 1702 (1935).

[3] R. G. Dickinson and J. L. Carrico, *ibid.*, **56**, 1475 (1934).

[4] K. L. Müller and H. J. Schumacher, *Z. physik. Chem.*, **35B**, 285 (1937).

[5] K. L. Müller and H. J. Schumacher, *ibid.*, **35B**, 455 (1937).

[6] C. Schott and H. J. Schumacher, *ibid.*, **49B**, 107 (1941).

[7] R. Schmitz and H. J. Shumacher, *ibid.*, **51**, 281 (1942).

[8] R. Schmitz and H. J. Schumacher, *ibid.*, **52**, 72 (1942).

[9] H. J. Schumacher, *Angew. Chem.*, **53**, 501 (1940).

[10] F. S. Dainton, D. A. Lomax and M. Weston, *Trans. Faraday Soc.*, **53**, 460 (1957).

[11] J. Adam, P. Goldfinger and P. A. Gosselain, *Bull. soc. chim. Belg.*, **65**, 549 (1956).

[12] J. R. Lacher, J. J. McKinley, C. H. Walden, K. R. Lea and J. D. Park, THIS JOURNAL, **71**, 1334 (1949).