

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

CHAIN REACTIONS PRODUCED BY LIGHT AND BY ALPHA RADIATION¹BY HUBERT N. ALYEA²

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"Ion cluster" mechanisms, postulated for reactions taking place under alpha particle bombardment, could not explain the hydrogen-chlorine reaction.³ Here the secondary step was an atomic chlorine chain, as in the corresponding photochemical reaction.⁴ Inasmuch as no other photochemical chain reactions had ever been studied under alpha particle bombardment, such a comparison seemed timely, to ascertain how generally a chain mechanism, instead of ion clustering, might succeed the initial process of alpha particle ionization. The criterion for such a chain process would be a large number of molecules reacting per ion pair produced, and this, in turn, should be compared with the corresponding photochemical yield.

This was done for the reactions of (1) **the hydrogen-chlorine combination**,⁴ and (2) **the synthesis of phosgene from carbon monoxide and chlorine**.⁵ The reader is referred to the citations, where experimental methods and results for these two reactions under both light and alpha radiations are discussed in detail.

(3) **The Chlorination of Benzene**.—C. p. benzene saturated with chlorine was sealed in a tube together with a thin capillary containing a known amount of radon. Nitrogen was bubbled into the tube before sealing, although the benzene still contained a certain amount of dissolved atmospheric oxygen which was not removed. The tube was shaken momentarily to break the capillary, which distributed radon throughout the solution, and it was then allowed to stand in the dark for several hours, by which time all of the chlorine had reacted. Blank runs were likewise made. The formation of hexachlorobenzene was measured by titration of the free chlorine with standard thiosulfate solution⁶ at the beginning and conclusion of a run. A typical run with 0.0046 curie of radon gave 1.4 millimoles of chlorine in 20 cc. of benzene reacted in one hour. This represents a total of 6.06×10^{20} (= the number of chlorine molecules in one millimole of

¹ I am indebted to Professor S. C. Lind for his kindly interest and helpful suggestions during this research.

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³ S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Co., New York, 1928, American Chemical Society Monograph No. 2, 2d ed., p. 139.

⁴ S. C. Lind and R. S. Livingston, *THIS JOURNAL*, **52**, 593 (1930). See also F. Porter, D. C. Bardwell and S. C. Lind, *ibid.*, **48**, 2603 (1926).

⁵ H. N. Alyea and S. C. Lind, *ibid.*, **52**, 1853 (1930).

⁶ A. Slator, *Z. physik. Chem.*, **45**, 540 (1903).

chlorine) $\times 1.4/60 \times 60 \times 3$ (since three chlorine molecules are consumed to give one molecule of hexachlorobenzene) $= 7.9 \times 10^{16}$ molecules formed per second $= M$. While Rn and RnA attain equilibrium quickly and had exerted practically full ionizing activity during the one-hour reaction period, RaC' was able to contribute only about 15% of the ionization it normally causes at equilibrium. This effect is allowed for by assuming only 2.15 instead of 3.0 sets of alpha particles from the original radon. Using these values, N = the number of alpha particles per curie of radon \times radon concentration in curies \times the number of ions produced by one alpha particle $= (2.15 \times 3.72 \times 10^{10}) \times (0.0046) \times (2.37 \times 10^5 \times 1.30)$, assuming the specific ionization of the mixture to be 1.30; or $N = 1.1 \times 10^{14}$. Therefore

$$\frac{M_{\text{C}_6\text{H}_6\text{Cl}_6}}{N_{\text{C}_6\text{H}_6\text{Cl}_6 + \text{C}_6\text{H}_6 + \text{Cl}_2}} = 7.9 \times 10^{16} / 1.1 \times 10^{14} = 720$$

In similarly conducted experiments by Luther and Goldberg,⁷ a minimum photochemical chain length of 75 is indicated by the fact that the photochemical rate is that many times slower in the presence of oxygen, an inhibitor.⁸ From the nature of the induction period which they obtained, it can be conjectured that the actual photochemical chain length is probably rather large, although no definite value can be assigned to it in this note.

(4) **Oxidation of Sodium Sulfitc in Solution.**—The photochemical measurements have been previously described⁸ and consisted in shaking 20 cc. of 0.6 molar aqueous sulfite solution in a bottle filled with oxygen. The sulfite disappearing was determined titrimetrically at the end of the shaking period. For the alpha-particle reaction the experimental procedure was identical, but in addition a thin capillary containing a known quantity of radon was placed in the sulfite solution. Immediately upon beginning to shake, the capillary broke and distributed the radon throughout the system. In the absence of radon 1.40 millimoles of sodium sulfite oxidized in five minutes; 0.0043 curie of radon increased the rate 0.20 millimole. The calculation of M/N carried out as above for the chlorination of benzene yields a chain length greater than 5000 molecules per ion pair produced.

Exponentially following each yield in the table is a reference to the original source of the value quoted. The yield 200,000 has no great significance in itself, since it depends on the purity of the gases. Of greater importance is, that simultaneous measurements on the same gas mixture give a ratio of $M/N:M/h\nu$ of 1:1. The same ratio is also obtained for the phosgene synthesis. Here, an additional factor makes the absolute value of 5000 of still less importance: the yield depends on the intensity of the radiation, and under more favorable conditions has been as high as 85,000 molecules

⁷ R. Luther and E. Goldberg, *Z. physik. Chem.*, **56**, 43 (1906).

⁸ H. N. Alvea and H. J. Bäckström, *THIS JOURNAL*, **51**, 90 (1929).

TABLE I
RESULTS OF EXPERIMENTS

Reaction studied	Calculation of M/N values on the basis of	M/N Alpha reaction	$N/h\nu$ light reaction
(1) $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$	$M_{\text{HCl}}/N_{\text{H}_2 + \text{Cl}_2}$	200,000 ⁴	200,000 ⁴
(2) $\text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2$	$M_{\text{COCl}_2}/N_{\text{CO} + \text{Cl}_2}$	5,000 ⁵	5,000 ⁵
(3) C_6H_6 (liq.) + $3\text{Cl}_2 \longrightarrow \text{C}_6\text{H}_6\text{Cl}_6$	$M_{\text{C}_6\text{H}_6\text{Cl}_6}/N_{\text{C}_6\text{H}_6\text{Cl}_6 + \text{Cl}_2 + \text{C}_6\text{H}_6}$	> 700 ⁹	large ⁷
(4) Na_2SO_3 (soln.) + $\frac{1}{2}\text{O}_2 \longrightarrow \text{Na}_2\text{SO}_4$	$M_{\text{Na}_2\text{SO}_4}/N_{\text{H}_2\text{O} + \text{Na}_2\text{SO}_3 + \text{Na}_2\text{SO}_4}$	> 5,000 ⁹	100,000 ⁸

M/N = number of molecules formed per ion pair produced.

$N/h\nu$ = number of molecules formed per quantum absorbed.

per ion pair. The values 700 and 5000 are only semi-quantitative, the impurities in the materials and experimental errors being much greater in the alpha-particle runs. For this reason, the M/N values have been calculated for Reactions 3 and 4 by assuming that all questionable factors are operating in that direction which would lead to shorter chains. Thus, in calculating N , it is assumed that ionization not only of the reactants, but of the products as well¹⁰ leads to reaction. The M/N value so derived represents a minimum chain length; more accurate determinations with carefully purified materials might give a much *larger* yield per ion pair (and undoubtedly would), but certainly no *smaller*.

The results point undeniably to the fact that in these four photochemical chain reaction, alpha-particle bombardment gives rise to chains instead of ion cluster reactions. No doubt many other photochemical chain reactions would give analogous results, and we wish in particular to emphasize this as another method for the identification and study of chain reactions.

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⁹ Values taken from data in this paper.

¹⁰ Compare the decomposition of hydrogen iodide in aqueous solutions by radon. S. C. Lind, *Le Radium*, **8**, 289 (1911); and by β - and γ -rays, Kailan, *Sitzb. Akad. Wiss. Wien*, **121**, 1351 (1912).