

707. *Photochlorination. Part I. The Photochlorination of Toluene Vapour.*

By MOWBRAY RITCHIE and W. I. H. WINNING.

Reaction between chlorine and toluene vapour has been observed to take place at 25°, thermally and under the action of light of wave-lengths 3650 and 4060 Å. Both reactions were rapid and both were inhibited by oxygen. Vessel surface effects are considered to play an important part.

Quantum-efficiency determinations have shown that the effect of oxygen may be expressed by an equation of the type $\gamma_{Cl_2} = a/(b + [O_2])$. The thermal reaction is similarly inhibited, but to a greater degree.

The thermal reaction obeys a second-order relationship, in agreement with the postulate of benzyl chloride and hydrogen chloride as the sole products for the conditions concerned.

The presence of the thermal reaction allows only an indirect measure of the quantum efficiency of the oxygen-free photo-reaction to be made. Such quantum efficiency for the conditions involved is of the order 8×10^4 .

In a projected comparison of the kinetics of the hydrogen-chlorine photoreaction (Ritchie and Taylor, *Proc. Roy. Soc.*, 1942, *A*, **180**, 423) with other photochlorinations, attention has been directed to the photochlorination of toluene vapour. Satisfactorily reproducible results were difficult to obtain under comparable experimental conditions, mainly because of the existence of a rapid thermal dark reaction strongly influenced by surface action, but the observations are here recorded since previous investigation of such chlorination has generally been confined to the liquid state.

TABLE I.
Vessel volume, 1 litre. Temp., 20°. $\lambda = 4060 \text{ \AA}$.

Cl ₂ , mm. (initial).	Toluene, mm. (initial).	O ₂ , mm.	t, sec.	ΔCl_2 , mm.	ΔHCl , mm.	$10^{-3}\gamma_{\text{HCl}}$
25.3	17.3	—	300	7.5	7.5	0.9
25.5	17.4	—	300	3.8	3.9	0.5
25.9	16.2	—	300	12.1	12.5	1.5
25.3	16.6	—	200	6.9	7.3	1.4
25.4	17.7	—	200	16.6	16.7	3.1
25.0	17.3	—	120	13.4	15.5	4.8
25.0	17.0	—	85	12.1	13.0	5.7
25.0	17.0	25.0	600	0.0	0.0	0.0
25.0	17.0	3.0	1800	1.0	1.1	0.023
25.0	17.0	1.0	3600	2.2	3.9	0.040
Thermal reaction.						
25.0	17.0	—	600	0.0	0.0	—
25.5	17.2	—	900	5.0	3.0	—
25.5	17.2	—	900	6.6	5.6	—

Preliminary work by Taylor (Thesis, 1941, University of Edinburgh), with light of wave-length 4060 \AA ., and with initial pressures of toluene and chlorine of 17 and 25 mm. of mercury, respectively, at 20°, in a spherical glass 1-l. vessel showed that photochlorination was rapid and of high quantum efficiency. After an exposure, residual chlorine was determined by standard thiosulphate after addition of 20 ml. of 20% potassium iodide solution; the further addition of 20 ml. of saturated potassium iodate solution gave additional iodine corresponding to the amount of hydrogen chloride formed during the illumination. Some of these preliminary results are quoted, in the order in which they were obtained, in Table I, where ΔCl_2 and ΔHCl represent the changes in pressure in the times stated. The values of quantum efficiency of hydrogen chloride formation (γ_{HCl}) are approximate only, and were based on the previous calibrations of Ritchie and Taylor (*loc. cit.*). Three experiments in which oxygen was added, and three determinations of the accompanying thermal reaction, are also given.

It will be observed that the pressure of hydrogen chloride produced is approximately equal to the decrease in chlorine pressure; the photo-reaction is of high quantum efficiency, but is markedly retarded by oxygen: the thermal reaction is relatively small. Although the results are somewhat erratic, this being attributed to the disturbance of the system after each illumination, the photochemical rate of chlorination increases generally with repeated experiment.

It was, therefore, decided to investigate such reaction more fully under experimental conditions of vessel size, wave-length, and light intensity similar to that of the hydrogen-chlorine reaction above mentioned, and to use the inhibiting effect of oxygen as a means whereby the chlorine concentration might be measured photometrically at the end of a period of oxygen-free illumination. The general procedure was similar to that given by Ritchie and Taylor. Chlorine and sulphur-free toluene were purified by repeated distillation, by means of liquid air, as required. The cylindrical silica reaction vessel was of 32 ml. volume.

The Effect of Oxygen.—A complication immediately became evident in that even in the presence of oxygen an appreciable thermal reaction occurred, of a magnitude much greater than that expected on the basis of the above preliminary experiments with the litre vessel. The first observations indeed showed only a slight thermal reaction, but with continued experiment such reaction increased progressively in rate until it amounted finally to as much as 70% of the total reaction. Rates then became approximately constant, and the results given subsequently refer to such conditions.

Addition of oxygen to a pressure greater than 60 mm. rendered the overall rate so slow that investigation of the effect of oxygen above this pressure was carried out with the full light of the mercury-vapour lamp, filtered through 3 cm. of 5% copper sulphate solution, in a glass vessel. Results are given in Table II, where absolute quantum efficiencies of chlorine removal have been calculated on the assumptions that (a) the thermal and photochemical reactions are additive, (b) the quantum efficiency at 60 mm. oxygen pressure is the same for the "full" light as for light of 4060 \AA . In all experiments, 300 mm. of oxygen were added finally to reduce the rates to such a low value that the residual chlorine concentration could then be determined photometrically by means of light of wave-length 3650 \AA .

In these experiments where the pressure of oxygen was increased from 130 to 450 mm., the thermal reaction decreased from 16 to zero percentage of the total.

TABLE II.
Temperature 25°; $t = 1200$ secs.

O ₂ , mm.	$\gamma = 4060 \text{ \AA.}$					" Full " light.					
	Toluene, mm. (initial).	Cl ₂ , mm. (initial).	Final Cl ₂ (total).	Final Cl ₂ (thermal).	γ_{Cl_2}	O ₂ , mm.	Toluene, mm. (initial).	Cl ₂ , mm. (initial).	Final Cl ₂ (total).	Final Cl ₂ (thermal).	γ_{Cl_2}
3.5	15.1	29.9	16.5	21.1	22.9	60	15.2	30.0	14.9	26.6	5.5
5	15.0	29.8	19.4	23.3	18.2	130	15.0	30.4	17.2	28.2	4.9
10	15.2	30.1	22.2	24.9	12.0	200	15.2	30.1	18.2	28.8	4.7
30	14.9	29.7	23.5	25.3	7.9	300	14.8	30.0	20.3	29.4	3.9
60	15.1	30.3	25.3	26.6	5.5	450	15.0	30.4	23.6	30.4	2.7

Although the mean chlorine and toluene concentrations are not respectively identical in each experiment, quantum efficiencies tend to become inversely proportional to oxygen pressure at the higher pressures. Quantum efficiencies may be expressed approximately by the equation $\gamma_{Cl_2} = a/(b + [O_2])$ over the oxygen range 10—450 mm.; efficiencies calculated in this way, with $a = 2000$ and $b = 245$, are compared with the experimental values in Table III.

TABLE III.

O ₂ , mm.	10	30	60	130	200	300	450
$\gamma_{exp.}$	12.0	7.9	5.5	4.9	4.7	3.9	2.7
$\gamma_{calc.}$	7.9	7.3	6.5	5.3	4.5	3.7	2.9
$\gamma_{exp.}/\gamma_{calc.}$	1.5	1.1	0.85	0.93	1.04	1.05	0.93

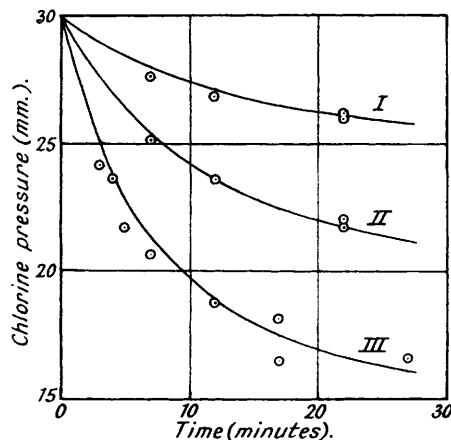
Thermal Reaction in the Oxygen-free System.—After addition of toluene vapour to a pre-determined pressure, 30 mm. of chlorine were added as rapidly as possible. This operation took normally 1—2 minutes, care being necessary to prevent damage to the Bourdon gauge. When the thermal reaction had proceeded for various times, zero time being fixed arbitrarily as the time when chlorine addition was complete, oxygen to a pressure of 300 mm. was added, and the residual chlorine determined photometrically. During the thermal reaction, the pressure remained substantially constant, only a small decrease (less than 1 mm.) being observed. Three series were carried out, with initial pressures of toluene of 5, 10, and 15 mm. Results are shown graphically in the figure, where curve I refers to an initial toluene pressure of 5 mm., curve II to 10 mm., and curve III to 15 mm.

In each series, the decrease in chlorine pressure finally approaches, but never exceeds, the initial toluene pressure, in agreement with the mono-substitution reaction: $C_6H_5 \cdot CH_3 + Cl_2 = C_6H_5 \cdot CH_2Cl + HCl$. Pressures of toluene were calculated for various times on this basis. It was then found that the rate of decrease of chlorine pressure could be satisfactorily expressed by the second-order equation:

$$-d[Cl_2]/(dt) = k[Cl_2][C_6H_5 \cdot CH_3]$$

The continuous curves of the figure have been constructed by means of the standard bimolecular formula, with pressures in mm. and with $k = 0.0026$ for curve I, 0.0033 for curve II, 0.0050 for curve III; in such calculations 2 minutes were added to the standard zero time, this allowing for the appreciable reaction which took place during the addition of chlorine. The bimolecular constant increases with increased initial pressure of toluene.

Total Reaction in the Oxygen-free System.—From the figure it is obvious that during such chlorine addition, thermal reaction had occurred to the extent of approximately 30% of the total, a change too large to permit the application of the usual methods of examination of the photoreaction. The following observations were, however, recorded. To 15 mm. of toluene, 30 mm. of chlorine were added as rapidly as possible, and light of wave-length 3650 \AA. then applied. The rate of chlorine disappearance was then followed by recording the movement of the light spot of the photo-electric cell-galvanometer system. The values of chlorine



pressure thus obtained were regarded as reasonably accurate after 2 minutes. Typical results are presented in Table IV, where the given rates of chlorine removal were obtained from the smoothed curve of chlorine pressure plotted against time.

TABLE IV.

Total reaction.

$\gamma = 3650 \text{ \AA}$. Initial toluene pressure = 15.0 mm. Initial chlorine pressure = 30.0 mm.
Temp. = 25°.

t , mins.	0	1	2	3	4	5	6	7	8	10
Cl_2 , mm.	(30)	(9.5)	(5.5)	3.2	2.4	1.8	1.6	1.3	1.2	1.2
$d[\text{Cl}_2]/dt$	(16.6)	(8.8)	(3.2)	1.7	0.7	0.4	0.2	—	—	—
$\log_{10} d[\text{Cl}_2]/dt$	(1.22)	(0.945)	(0.50)	0.23	-0.15	-0.40	-0.7	—	—	—

An estimate of the photochemical quantum efficiency may be made as follows. The plot of $\log_{10} d[\text{Cl}_2]/dt$ against time is almost exactly linear; extrapolation to zero time gives a value of $\log_{10} d[\text{Cl}_2]/dt$ of 1.22, corresponding to a total thermal plus photochemical rate of chlorine removal of 16.6 mm. per minute. From the previous section, the approximate thermal reaction rate at "zero" time is $k[\text{Cl}_2][\text{C}_6\text{H}_5\cdot\text{CH}_3] = 0.0050 \times 25 \times 10 = 1.25$ mm. per minute. If the thermal and the photo-reaction be regarded as additive, the rate of the photo-reaction alone is then 16.6—1.2 = 15.4 mm./min. For the conditions in question, from previous calibration, the intensity of absorbed light of wave-length 3650 \AA . was 8.6×10^{14} quanta per sec. and the corresponding quantum efficiency at this intensity at a chlorine pressure of 25 mm. and a toluene pressure of 10 mm. is estimated as 7.5×10^4 molecules of chlorine per quantum absorbed. On the assumption of a mutual recombination process in the mechanisms of both thermal and photo-reactions (cf. Noyes and Leighton, "Photochemistry of Gases," 1941, p. 198), the corresponding efficiency is 8.1×10^4 .

In contrast to the purely thermal reaction, the recorded chlorine pressures of Table IV show that monosubstitution is by no means the only reaction occurring; the original pressure increase on illumination due to the heat of reaction (22,000 calories) was succeeded by a continuous decrease in pressure, and reaction was accompanied finally by the production in the reaction vessel of a yellowish deposit, soluble in alcohol.

DISCUSSION.

An early investigation by Luther and Goldberg (*Z. physikal. Chem.*, 1906, **56**, 43) on photo-reactions of chlorine with various organic substances in the gaseous state, including toluene, showed that oxygen exerts a strong retarding influence. Gibbs and Geiger (U.S.P. 1,246,739, 1917) describe a process in which toluene vapour with various proportions of chlorine may be used to produce benzyl chloride, benzylidene chloride, or benzotrichloride by irradiation by ultra-violet light, a somewhat similar process being given by Ellis (U.S.P. 1,202,040, 1918).

With liquid toluene, chlorinated just below the boiling point, Book and Eggert (*Z. Elektrochem.*, 1923, **29**, 521) found benzyl chloride to be almost the sole product, in addition to hydrogen chloride, no matter whether the reaction was carried out in light or in darkness, provided that no chlorine "carriers" were present. At a temperature of -80° , the dark reaction was almost entirely suppressed, but suitable illumination gave benzyl chloride and chlorotoluene, with a quantum efficiency of about 25 molecules. Further work by Bergel (*Ber.*, 1926, **59**, 153) and by Olivier (*Rev. Trav. chim.*, 1938, **57**, 741) suggested that the compounds formed and their proportions depend on the intensity of the light used, the latter author postulating derivatives of chlorocyclohexanes as possible other products.

Kharash and Berkman (*J. Org. Chem.*, 1941, **6**, 810), working with liquid chlorine and liquid toluene, found, both in the dark reaction and in the much more rapid reaction brought about by illumination, that of the 99% of chlorine reacting 54% was used by substitution in the side chain and 45% by addition to the nucleus. Oxygen appeared to retard the reaction only to a small degree.

As shown by the results quoted above, detailed examination of the kinetics of photochlorination of toluene vapour cannot be satisfactorily carried out for the present conditions by reason of the accompanying thermal reaction. Mason, Small, Thompson, and Wheeler (*J.*, 1931, 3150) investigated the vapour-phase thermal reaction between chlorine and toluene at temperatures above 250° , by means of a flow system; reaction proceeded smoothly and rapidly to give side-chain chlorination products, mainly benzyl and benzylidene chlorides, but in the presence of small amounts of chlorine carriers such as iodine or ferric chloride nuclear substitution

also occurred. When the reaction tube was packed with fire-clay, practically complete chlorination was obtained at 250° with a gas mixture of 1 vol. of chlorine to 1.2 vols. of toluene; the proportional formation of benzylidene chloride was greatly increased with excess of chlorine at 300°. Since the technical object sought was complete utilisation of the chlorine, comparison with the present results at 25° as to absolute rates is difficult, more particularly as surface action is obviously involved in both cases. The equivalence of the original toluene pressure and the total chlorine pressure change, the applicability of the bimolecular law, and the constancy of pressure, all point to benzyl chloride and hydrogen chloride as the sole products of the present thermal reaction. Such reaction is retarded by oxygen; from Table II rates of the thermal reaction in relation to oxygen pressure are as follows:

Temp. = 25°. Initial toluene pressure = 15.0 mm. Initial chlorine pressure = 30.0 mm.
t = 20 mins.

O ₂ , mm.	3.5	5	10	30	60	130	200	300	450
ΔCl ₂ (exp.)	8.8	6.5	5.2	4.4	3.5	2.2	1.3	0.6	0.0
ΔCl ₂ (calc.)	8.8	8.3	7.1	4.5	2.9	1.6	1.1	0.77	0.5

Although the mean chlorine and toluene pressures are not respectively constant throughout, the retardation by oxygen can be fairly well expressed by the equation $\Delta[\text{Cl}_2]_{\text{calc.}} = 250/(25 + [\text{O}_2])$. Values thus calculated are given in the third line of the above table; retardation by oxygen is much more efficient than in the case of the photo-reaction.

In the absence of oxygen it is obvious that benzyl chloride is by no means the only substitution product; with initial pressures of 30 mm. of chlorine and 15 mm. of toluene, practically all the chlorine was used up in 5 minutes with the light intensity concerned.

THE UNIVERSITY OF EDINBURGH.

[Received, August 9th, 1950.]