67. *The Photo-change of* N-*Chloroacetanilide in Various Solvents.*

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The transformation of *N*-chloro- into *p*-chloro-acetanilide was first studied by Chattaway and Orton (J., 1899, **75**, 1046; 1900, **77**, 134, 152, 789, 797; 1901, **79**, 254). Armstrong (J., 1900, **77**, 1047) found that the presence of hydrogen chloride was essential for the reaction to take place, and Blanksma (*Rec. trav. chim.*, 1902, **21**, 366; 1903, **22**, 290) noted that light greatly accelerated it. Orton and Jones (*Rep. Brit. Assoc.*, 1910, 85) found that two distinct stages were involved,

$$\mathrm{NPhClAc} + \mathrm{HCl} \longrightarrow \mathrm{NHPhAc} + \mathrm{Cl_2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{NHPhAc} + \mathrm{Cl_2} \longrightarrow \mathrm{NHAc{\cdot}C_6H_4Cl} + \mathrm{HCl} \quad . \quad . \quad . \quad . \quad (2)$$

and Soper (*J. Physical Chem.*, 1927, **31**, 1192) showed that the speed of transformation is approximately equal to that of (2).

Mathews and Williamson (*J. Amer. Chem. Soc.*, 1923, **45**, 2574) found that in the light of a quartz mercury-vapour lamp the reaction took place in the absence of added hydrogen chloride in benzene and some other solvents. From the last result it appeared that the photo-reaction in inert solvents might be a simple isomerisation, and that the relative velocities might throw some light on solvent effect and its relation to the physical properties of the solvent.

The electrical environment of the solute appears to be more likely than any other cause to influence its reactivity, and it is the polar or non-polar nature of the solvents which has been most frequently considered in this connexion. In general, it has been concluded that in thermal reactions velocity is greater in the more polar solvents, but in photo-reactions, *e.g.*, the polymerisation of anthracene (Winther, *Trans. Faraday Soc.*, 1926, **21**, 595) and the oxidation of iodoform (Plotnikow, *Z. physikal. Chem.*, 1911, **76**, 743), there is some evidence that velocity decreases with increasing polarity.

The results now obtained point in the same direction; for instance, in the simple benzene solvents velocities were in the order $\mathrm{Ph{\cdot}CH_3} > \mathrm{PhH} > \mathrm{PhCl} > \mathrm{PhBr}$, and it is significant that this order is the same as that found by Rule and Mitchell (J., 1926, 3202) for the increase of rotatory power of certain esters in the same solvents.

In solvents such as *cyclo*hexane and decalin the main product is acetanilide; so reaction evidently occurs between solvent and solute in these cases and the normal reaction is suppressed.

The relation between the velocity of a reaction and the cohesion of the medium has been studied by Soper and Richardson (J., 1929, 1873). From their own measurements on the reaction between *N*-chloroacetanilide and hydrochloric acid in aqueous solution, the cohesion of which was varied by the addition of other substances, and from results obtained by other workers, they concluded that, when the products of a reaction have greater cohesion than the reactants, then solvents of high cohesion cause an acceleration. Conversely, if, as in the case examined, the products are of lower cohesion than the reactants, then such solvents retard.

In attempting to correlate this and other physical properties of the solvent with changes in velocity of reaction, there appeared to be a simple relation for benzene and the mono-halogeno-benzenes, in which velocity decreases with an increase in cohesion and in density. However, in toluene, *cyclo*hexane, and decalin no such relation could be observed, possibly because these solvents themselves undergo reaction with the chloroamine (see p. 242); carbon tetrachloride, too, did not conform to the relationship.

EXPERIMENTAL.

Preparation of N-*Chloroacetanilide.*—The following details, kindly supplied by the late Professor Orton, do not appear to have been published. 50 G. of finely powdered $NaHCO_3$ were added in small portions and with continuous shaking to 450 c.c. of filtered 0·5*N*-bleaching powder aq., and the pptd. $CaCO_3$ was removed. 13·5 G. of acetanilide were dissolved in 700 c.c. of hot water, and obtained as a fine suspension by rapid cooling to 30° with thorough shaking. The hypochlorite solution was then added in portions (20 min.) to the warm anilide suspension, shaken during the addition and for further 30 min. thereafter; the pptd. cryst. solid, which should be quite white, was separated, pressed, stirred with about 100 c.c. of H_2O, and immediately recovered and dried over P_2O_5 and anhyd. K_2CO_3 in a vac. desiccator (yield, 14 g. of 98—100% purity). Exposure to strong light should be avoided during the prepn., a glass spatula used, and the product kept in the dark.

Purification of Solvents.—Commercial benzene was purified by treatment with conc. H_2SO_4, alkali, and H_2O in the usual way, shaken with $CaCl_2$, set aside for 2 days, and fractionated; the middle fraction was dried over P_2O_5 and again fractionated. For more intensive drying it was refluxed for 3 hr. over Na and distilled into the reaction vessel as required. For all the later work, B.D.H. benzene, " pure for molecular weights," was dried over $CaCl_2$ and fractionated.

All the other solvents used were specially purified B.D.H. reagents, which were dried over $CaCl_2$ and fractionated. Further purification made no difference to the results.

Effect of Solvent on Velocity.—Radiation was obtained by means of a Hewittic Hg-vapour lamp, and in the first stage of the work no attempt was made to measure the intensity of the radiation. Current was obtained from the 100-volt mains and the lamp was connected in series with an adjustable resistance so arranged that a const. current of 3·75 amp. at 70 volts passed through the lamp. The constancy of the voltage was checked by means of a voltmeter connected to the lamp terminals. Monochromatic radiation was obtained by filtering the radiation through Chance's ultra-violet glass, which allows little else to pass than the light giving the strong Hg line, 3659 Å. In order to eliminate infra-red radiation, the light was passed through a 2-l. flask containing very dil. $CuSO_4$ aq., which also served as a condenser. A parallel beam, obtained by means of a 100-c.c. glass flask filled with H_2O, was directed through the thermostat and reaction vessel. The thermostat was a rectangular zinc vessel, 8″ × 3″ × 4″, into which quartz windows were cemented back and front. (The use of quartz was not essential, since the wave-length employed was transmitted by glass; but for shorter wave-lengths glass cannot be used.) The temp. was maintained const. by means of an immersion heater and a Hg thermo-regulator electrically controlled.

The reaction vessel consisted of a cylinder 6 cm. in diam. and 3 cm. in length, on the ends of which were sealed quartz discs.

It was assumed that the lamp was giving a const. intensity provided that the current was const., and this probably was so when the lamp was new. Slight readjustments made appreciable differences in velocity coeffs., and where comparisons are given, expts. were carried out under identical conditions.

In the first measurements 0·15—0·8 g. of the chloro-amine was dissolved in 50 c.c. or 100 c.c. of C_6H_6, the actual concn. of the solution being checked iodometrically in one portion. The remainder of the solution was kept in the thermostat at 23·2° for 10 min., and then exposed to the radiation, 5 c.c. being withdrawn at intervals and titrated.

Runs were carried out in C_6H_6 which was (*a*) ordinary pure liquid, (*b*) satd. with H_2O, and (*c*) intensively dried over Na and distilled thence into the reaction vessel. The rate of change was the same in all cases: in (*a*) and (*b*) the quantities changed in the first 75 min. were (*a*) 62·4%, (*b*) 62·8%, and in (*c*), reckoning from the time when reaction started, 62·5%. In (*a*) and (*b*) reaction began as soon as the solutions were irradiated, but in (*c*) there was an induction period of 20 min. In a repetition of (*c*) there was no reaction for 30 min.

A series of determinations in various solvents was now carried out as follows. A weighed quantity of the chloroamine was dissolved in 100 c.c. of the solvent, and the solution standardised; portions of 20 c.c. were submitted to radiation for varying periods, and then titrated as before. These determinations were made at two temps. and show fair consistency in the results, although such exact values as are obtained in an ordinary thermal reaction are not to be expected. Typical results are shown in Table I, k being calculated from the formula $k = 1/t \cdot \log c_1/c_2$, t being in min. and c_1 and c_2 in g.-mol./l.

TABLE I.

Solvent, dry benzene. Temp., 29·5°. λ = 3659 Å.

Chloroamine = 0·057 g.-mol./l.			Chloroamine = 0·0115 g.-mol./l.		
t.	Titre (N/10-$Na_2S_2O_3$).	$k \times 10^5$.	*t*.	Titre (N/20-$Na_2S_2O_3$).	$k \times 10^5$.
0	22·8	—	0	9·24	—
8	20·9	587	15	8·60	481
15	20·2	569	20	8·34	513
20	19·8	525	30	8·00	481
30	19·0	488	50	7·25	532
	Mean	542		Mean	502

Other results are as follows:—

Solvent.	Temp.	*c*.	$k \times 10^5$. Max.	Min.	Mean.
Benzene	29·5°	0·057	592	573	583
,,	29·5	0·0123	504	474	483
,,	22·2	0·049	357	289	331
,,	23·6	0·014	359	290	339
Chlorobenzene	29·5	0·050	393	350	377
Bromobenzene	29·5	0·044	327	279	308
Toluene	23·6	0·0085	1948	1895	1928

These results were not considered sufficiently accurate for the calcn. of temp. coeffs., owing to variations in the intensity of the radiation. A series of comparisons was therefore made at two temps. but with the lamp running during the whole time for each solvent. The results at 23·6° and 33·6° were as follows:—

Solvent	C_6H_6	C_6H_5Cl	C_6H_5Br	$CHCl_3$
$10^5 \cdot k_{33\cdot6^\circ}$	513	382	301	319
$10^5 \cdot k_{23\cdot6^\circ}$	382	291	233	238
Coeff.	1·34	1·31	1·29	1·34

Figures determined at a later stage from the quantum-efficiency values, *i.e.*, allowance being made for changes in intensity of the radiation, were essentially in agreement with the above. In CCl_4, *cyclo*hexane, and decalin there appeared to be no temp. coeff., and in toluene the value was negative.

Investigation of Reaction Products.—In all cases the irradiated liquids were analysed. In addition to the normal product, *viz.*, *p*-chloroacetanilide, other products were obtained in certain cases; these were (*a*) acetanilide, (*b*) chlorinated solvent, and (*c*) diacetylhydrazobenzene.

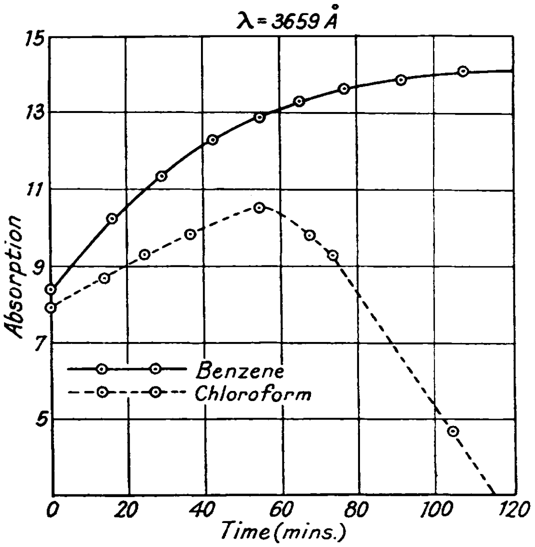
(*a*) Acetanilide was produced in reaction in toluene, *cyclo*hexane, and decalin; from the first it was obtained on concn., and from the other two it separated during reaction. A small quantity of *p*-chloroacetanilide was obtained on further concn. of the toluene solution, but none from *cyclo*hexane and decalin. No acetanilide was found in C_6H_6, chloro- or bromo-benzene, or $CHCl_3$.

(*b*) Fractional distillation of the liquid residues gave small quantities of chlorinated products from solvents containing hydrogen. From 150 c.c. of residual $CHCl_3$, about 1 c.c. of CCl_4 was obtained. Very small quantities of chlorinated products were separated from C_6H_6

(b. p. 140—180°), C_6H_5Cl (b. p. 170—180°), and C_6H_5Br (b. p. > 180°); larger quantities were obtained from toluene (b. p. 163—200°), *cyclo*hexane (b. p. 84—180°), and decalin (b. p. 200—235°).

(*c*) In all cases evaporation to dryness gave a minute quantity of coloured crystals as well as the main product. In two cases, from CCl_4 and C_6H_5Br, a few crystals were isolated (m. p. 105°); when mixed with diacetylhydrazobenzene (m. p. 105°) prepared by Schmidt and Schultze's method (*Annalen*, 1881, **207**, 327), they melted at 103°.

The presence of this compound was also demonstrated as follows. Pure $CHCl_3$ (50 c.c.) was irradiated for ½ hr.; 0·01 g. of the diacetyl compound was then added. This at first caused very strong absorption, followed by a slow *decrease* in absorption, thus resembling the results observed when the reaction itself was carried out in this solvent (see curve below). This decrease evidently indicates that some change takes place in this solvent but not in any other. It was found that hydrazobenzene when submitted to ultra-violet light in $CHCl_3$ undergoes the benzidine change, but that this does not take place in other solvents; hence, it would appear that in this case diacetylhydrazobenzene is first formed and then undergoes decomp., probably owing to the formation of HCl.



The concn. of HCl in solution was very small and could not be detected by alc. $AgNO_3$ immediately after reaction. A small quantity, however, was found after the solution had stood for some hours.

Quantum-efficiency Measurements.—The quantum efficiency of the reaction was determined in 8 solvents. The exptl. arrangements were modelled on those of Norrish (J., 1929, **1160**), the condensed radiation being passed through the reaction vessel into a photoelectric cell connected to a sensitive galvanometer. By noting the difference in deflexion when radiation was passed through (*a*) the pure solvent and (*b*) the solution of *N*-chloroacetanilide, the amount of energy absorbed could be calculated. The photoelectric cell was an Osram evacuated Na cell which was enclosed in a metal box. With complete insulation of the terminals const. readings were obtained and there was no "dark" current. A current from a dry battery at 18 volts was passed through the cell, the circuit being completed by a 10,000-ohm resistance and a Pye Granta galvanometer with moving coil, and having a resistance of 50 ohms.

The photoelectric cell was calibrated against a large-surface Moll thermopile, which was itself calibrated by means of a Leslie cube (cf. Norrish, *loc. cit.*). As a check on this result, a separate calibration of the thermopile was obtained by means of a carbon-filament lamp which had been standardised at the National Physical Laboratory. The results obtained were as follows:

(*a*) Leslie cube method: 1 cm. defln. = $35{\cdot}4 \times 10^2$ ergs/sec.
(*b*) Standard lamp method: 1 cm. defln. = $38{\cdot}1 \times 10^2$ ergs/sec.

Since (*b*) was considered to be the more accurate, this value was used in the calculations. For the calibration of the cell, the thermopile and the cell were mounted in turn so that the whole of the condensed radiation was either concentrated on the thermopile surface or passed through the window of the cell.

The following results were obtained:

Defln. with thermopile = 9·03 cm. (average of 9 readings).
Defln. with cell = 42·58 cm. (average of 15 readings).

Hence 1 cm. defln. for thermopile = 42·58/9·03 = 4·7 cm. for cell.

The method of irradiating the solution was the same as that already described, 40 or 60 c.c. being used at a time. The amount of absorption was measured at the moment of exposure, and again at intervals as the reaction proceeded. Contrary to expectation, it was found that in most cases the amount of absorption increases with time, although *p*-chloroacetanilide shows much weaker absorption at this frequency than *N*-chloroacetanilide. This appears to be due to the formation of a minute quantity of diacetylhydrazobenzene, which behaves as an internal filter. This increase of absorption was marked in C_6H_6, the halogen-substituted benzenes, and CCl_4; in $CHCl_3$ the absorption rises to a max. and then rapidly falls (see fig.). In toluene, *cyclo*hexane, and decalin the change is less marked, and acetanilide was the main product of the reaction.

Reaction is approx. proportional to the intensity *I*, as measured by the galvanometer deflexion, when radiation is passed through the pure solvent immediately before reaction. This is shown by the following results (λ = 3659 Å.) :

Solvent.	Temp.	*I*.	*k* × 10⁵.	*k* × 10⁵/*I*.	Solvent.	Temp.	*I*.	*k* × 10⁵.	*k* × 10⁵/*I*.
CH_6	15·6°	15·6	972	62·3	C_6H_5Cl	23·6°	8·70	364	41·8
,,	15·6	22·8	1460	64·0	,,	23·6	7·62	309	40·1
,,	15·6	20·33	1225	60·3	CCl_4	23·6	7·40	74·8	10·1
,,	15·6	8·04	423·7	52·7	,,	23·6	8·50	94·4	11·1

The velocity coeffs. indicated a unimolecular reaction in all cases, so that one coeff. calculated from titration at the end of each exposure should give a measure of the velocity throughout. The increase of absorption seems to be due to the formation of a very small quantity of an absorbing compound by a secondary reaction which does not sensibly affect the velocity of the main reaction. The following results are typical :

(1) Solution in C_6H_6; temp., 15·6°; 0·2 g. *N*-chloroacetanilide in 50 c.c. solvent; defln. through solvent = 22·8 cm.

Time	0	5	12	20	31	48·5	60	65
Deflexion	4·5	3·8	3·2	2·5	1·6	1·35	1·00	0·85
Absorption	18·3	19·0	19·6	20·3	21·2	21·8	21·8	21·95

Titration before exposure : 50 c.c. = 45·2 c.c. *N*/20-$Na_2S_2O_3$.
Titration after exposure : 50 c.c. = 17·5 c.c. ,,
k = (log$_e$ 45·2/17·5)/65 = 0·0146; *k* × 10⁵/*I* = 64·04.

(2) Solution in $CHCl_3$; temp., 15·6°; 0·2 g. *N*-chloroacetanilide in 50 c.c. solvent; defln. through solvent = 18·82 cm.

Time	0	14	28	48	53	70	82	87	91
Deflexion	8·2	7·4	6·7	5·6	6·0	8·9	9·9	10·1	10·35
Absorption	10·62	11·42	12·12	13·22	12·82	9·92	8·92	8·72	8·47

Titration before exposure : 50 c.c. = 45·2 c.c. *N*/20-$Na_2S_2O_3$.
Titration after exposure : 50 c.c. = 17·5 c.c. ,,
k = (log$_e$ 45·2/17·5)/91 = 0·01046; *k* × 10⁵/*I* = 56·5.

The reaction was carried out at 15·6°, 23·6°, and 33·6° and the results are in Table II. The first determinations were at 15·6° and these are likely to be less accurate than the later ones.

TABLE II.

Temp. 23·6°. *I* = Intensity of radiation as measured by galvanometer deflexion when radiation is passed through solvent. λ = 3659 Å.

Solvent.	*c*.	Time of exposure (min.).	*k* × 10⁵.	*I*.	*k* × 10⁵/I.	γ.
Benzene	1·932	20	509	9·23	54	29
,,	1·808	30	416	7·30	57	29
,,	3·616	30	396	8·60	46	33
,,	1·996	31	385	7·55	51	29
Chloroform	1·828	20	233	8·18	28	17
,,	2·016	45	204	8·20	25	17
Chlorobenzene	1·808	30	364	8·70	42	22
,,	1·954	32	309	7·62	41	22
Carbon tetrachloride	1·746	20	74·8	7·40	10	5
,, ,,	1·786	30	117·5	8·40	14	6
,, ,,	1·818	40	94·4	8·50	11	5
,, ,,	3·646	32	221·5	23·70	9·35	6
Decalin	1·808	21	2579	5·60	460	189
,,	1·819	20	2556	5·60	456	188
*cyclo*Hexane	1·890	23	2150	6·20	349	156
,,	1·868	20	2170	6·20	350	163
Toluene	1·694	33	1116	5·54	219	108
,,	1·694	31	1221	5·54	220	116
Bromobenzene	1·402	31	208	4·60	45	18
,,	1·350	35	180	4·60	40	16
,,	1·205	37	144	3·70	40	15
Carbon tetrachloride + 1 c.c. chloroform	1·996	30	—	5·00	—	13

For concns. of the same order as in Table II, the following values of $k \times 10^5/I$ were obtained at 15·6° and 33·6°.

	15·6°.	33·6°.		15·6°.	33·6°.
Benzene	64, 53, 60	66, 65	Decalin	407	457, 468
Chlorobenzene	—	56, 52	Toluene	69 *	163, 163
Chloroform	54, 41	33, 29	Bromobenzene	—	79, 83
*cyclo*Hexane	245, 297	344, 384	Carbon tetrachloride ...	—	13, 11, 10

* Unpurified toluene.

Calculation of Quantum Efficiency (γ).—In all cases the number of mols. of *N*-chloroacetanilide undergoing change for every quantum of energy absorbed has been calculated, the method being based on that of Rideal and Williams (J., 1925, **127**, 258). The following is a typical calculation, the results for 23·6° being given in the last col. of Table II, and those for 15·6° and 33·6° below.

Solvent, C_6H_6; temp. 23·6°; λ = 3659 Å.; 0·0998 g. of *N*-chloroacetanilide in 50 c.c. C_6H_6.

Before exposure, 10 c.c. = 19·2 c.c. $N/80$-$Na_2S_2O_3$. After exposure, 10 c.c. = 17·05 c.c. $N/80$-$Na_2S_2O_3$. Quantity exposed = 40 c.c.

$$\text{Molecules exposed} = \frac{40}{50} \times \frac{0{\cdot}0998}{169{\cdot}5} \times 6{\cdot}06 \times 10^{23} = 2{\cdot}855 \times 10^{20}.$$

Time, mins. = 31. $k = (\log_e 19{\cdot}2/17{\cdot}05)/31 = 0{\cdot}00385$.

Mols. changed in first second = $k/60$ × mols. present

$$= 0{\cdot}00385 \times 2{\cdot}855 \times 10^{20}/60 = 1{\cdot}83 \times 10^{16}.$$

Deflexion through solvent = 7·55 cm. Deflexion through solution = 3·20 cm. Absorption = 4·35 cm.

1 Cm. defln. on thermopile = 4·7 cm. on cell = $38{\cdot}08 \times 10^2$ ergs/sec.

Energy absorbed = $4{\cdot}35 \times 38{\cdot}08 \times 10^2/4{\cdot}7$ ergs/sec.

Quantum = $h\nu = 6{\cdot}55 \times 10^{-27} \times 8{\cdot}19 \times 10^{14}$.

$$\text{Quanta per sec.} = \frac{4{\cdot}35 \times 38{\cdot}08 \times 10^{15}}{4{\cdot}7 \times 6{\cdot}55 \times 8{\cdot}19} = 0{\cdot}06421 \times 10^{16}.$$

$$\gamma = 1{\cdot}83 \times 10^{16}/0{\cdot}06421 \times 10^{16} = 28{\cdot}5.$$

Solvent.	Value of γ.		Solvent.	Value of γ.	
	15·6°.	33·6°.		15·6°.	33·6°.
Benzene	38, 38, 27	34, 32	Decalin	129	178, 167
Chlorobenzene	—	28, 27	*cyclo*Hexane	117	180, 164
Chloroform	22, 26	22, 20	Toluene	34 *	107, 101
Bromobenzene	—	23, 22	Carbon tetrachloride ...	—	5·5, 5, 7

* Unpurified toluene.

Extent of Absorption.—The amount of absorption in different solvents, with the same concn. of the chloroamine, showed some variation. Thus, at 23·6° the substituted benzenes and C_6H_6 itself all give approx. the same values, the average percentages of the total absorption through the pure solvent being as follows: C_6H_6 58, C_6H_5Cl 59, $C_6H_5{\cdot}CH_3$ 56, C_6H_5Br 60. In CCl_4 it is 62, and *cyclo*hexane and decalin show about the same values, 71 and 74% respectively, whilst in $CHCl_3$ the low value of 47·3% is obtained. These values are little affected by temp.

Effect of Impurities.—The amount of absorption by the pure solvent itself was small and about the same in all cases, but in unpurified solvents the absorption may be much greater; *e.g.*, a specimen of unpurified toluene absorbed over 50% of the available radiation and the value of γ was correspondingly low.

In most cases the values of γ for any one pure solvent were fairly uniform, but there seems to be no reaction in the complete absence of H_2O. Contrary to the usual effect of impurities, addition of 2% of $CHCl_3$ to the solution in CCl_4 doubled the value of γ (Table II).

DISCUSSION OF RESULTS.

The development of colour as the reaction proceeds was noted by Orton and Grey (*Rep. Brit. Assoc.*, 1913, 136), who attributed it to either the formation of aniline or the presence of a tautomeric quinonoid substance. No evidence could be found in favour of either of these suggestions, but the demonstrated presence of traces of diacetylhydrazobenzene (p. 243) would account for both the colour and the increase of absorption.

Quantum Efficiency.—The high values for the quantum efficiency in all solvents point to some supplementary reactions which succeed a primary dissociation. All the following are possible. (ClMH is *N*-chloroacetanilide, HMCl is the *p*-chloro-compound, HMH is acetanilide, and MH is the radical ·NPhAc.)

$\mathrm{ClMH} + h\nu \longrightarrow \mathrm{ClMH}^{*} \longrightarrow \mathrm{Cl} + \mathrm{MH}$ .... (1)
$\mathrm{Cl} + \mathrm{MH} \longrightarrow \mathrm{MCl} + \mathrm{H}$ .... (2)
$\mathrm{H} + \mathrm{MCl} \longrightarrow \mathrm{HMCl}$ .... (3)
$\mathrm{H} + \mathrm{ClMH} \longrightarrow \mathrm{HMH} + \mathrm{Cl}$ .... (4)
$\mathrm{Cl} + \mathrm{HMH} \longrightarrow \mathrm{HMCl} + \mathrm{H}$ .... (5)
$\mathrm{Cl} + \mathrm{ClMH} \longrightarrow \mathrm{ClMCl} + \mathrm{H}$ .... (6)
$\mathrm{H} + \mathrm{ClMCl} \longrightarrow \mathrm{HMCl} + \mathrm{Cl}$ .... (7)
$\mathrm{Cl} + \mathrm{Cl} \longrightarrow \mathrm{Cl_2}$ .... (8)
$\mathrm{Cl} + \mathrm{H} \longrightarrow \mathrm{HCl}$ .... (9)
$\mathrm{MH} + \mathrm{MH} \longrightarrow \mathrm{HM{\cdot}MH}$ .... (10)

The occurrence of (4) and (6) would lead to the formation of reaction chains and an increased value for γ, although the effect should not be great owing to the low concentration of atomic hydrogen and chlorine. Again, the formation of hydrogen chloride would result in the usual reactions, $\mathrm{ClMH} + \mathrm{HCl} \longrightarrow \mathrm{HMH} + \mathrm{Cl_2}$; $\mathrm{Cl_2} + \mathrm{HMH} \longrightarrow \mathrm{HMCl} + \mathrm{HCl}$, which would probably account for the value $\gamma = 5$ (approx.) in carbon tetrachloride.

In solvents containing hydrogen the following additional reactions may occur, HS representing the solvent:

$\mathrm{Cl} + \mathrm{HS} \longrightarrow \mathrm{ClS} + \mathrm{H}$ . . . (11); $\mathrm{H} + \mathrm{ClMH} \longrightarrow \mathrm{HMH} + \mathrm{Cl}$ . . . (12)

and owing to the high concentration of the solvent these may become predominant, as they appear to be in toluene, decalin, and *cyclo*hexane, where acetanilide is the main product of the reaction. In these cases γ has very high values; it appears that reaction chains are produced and evidently extend outside the irradiated area. This accounts for complete reaction being obtained in *cyclo*hexane in 0·5 hour and for the continuation of reaction in all solvents after the source of radiation is removed.

SUMMARY.

1. The rate of change of *N*-chloroacetanilide under the influence of ultra-violet radiation ($\lambda = 3659$ Å.) has been measured in eight solvents.

2. The reaction does not take place or is very slow in the complete absence of water, but the velocity is not affected by a large increase in the quantity of water present.

3. Einstein's law is not followed in any solvent, but the lowest values were obtained in carbon tetrachloride, in which there is no possibility of reaction between solvent and solute.

4. Solvents containing hydrogen facilitate reaction by themselves reacting with atomic chlorine from the solute. This results in the formation of reaction chains and in some solvents appears to be the predominant factor in determining the velocity of change and the value of γ.

5. No general relationship between velocity and physical properties of the solvent was discernible, but in closely allied solvents reaction velocity diminishes with increasing dielectric constant, with increasing surface tension, and with increasing density.

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