

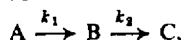
KINETICS OF THE PHOTOCHEMICAL CHLORINATION OF TRIMETHYLACETIC ACID*

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Abstract—The photochemical chlorination of trimethylacetic acid provides a typical example of competitive consecutive reactions of the type



in which the maximum obtainable concentration of intermediate B (chloromethyl dimethylacetic acid) is determined, by the ratio

$$\frac{k_1}{k_2}$$

Although no absolute values of k_1 and k_2 are determined their ratio is found to be 3.4/1.

Vapour phase chromatography, by which the reaction was followed, revealed the rather surprising presence of two different dichloro derivatives.

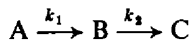
IR and NMR spectra proved that one of the dichloro derivatives contains a dichloro substituted methyl group.

This indicates the greater influence of resonance stabilization factors versus polar inductive effects in this photochemical chlorination reaction.

ALTHOUGH it is known that the presence of a carboxylic group retards the photochemical chlorination, the chlorination of trimethylacetic acid proceeds very easily, first to mono- and subsequently to dichlorotrimethylacetic acid.

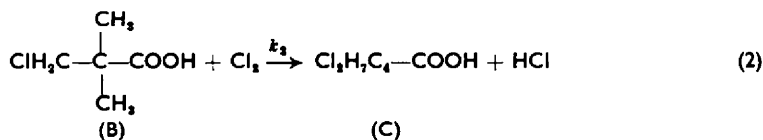
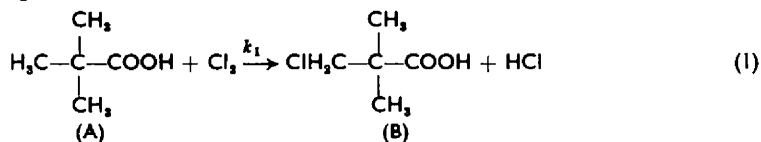
A. Kinetics

The parent compound (A) having 9 replaceable H-atoms, when subjected to chlorination, provides a typical example of a competitive consecutive reaction of the type



Since the production of the monochloro derivative (B) was of primary importance, a kinetic study of the chlorination reaction was undertaken.

The reaction sequence can be written as follows:



* Preliminary publication, *XIXth IUPAC Congress* London (1963); *Abstract* A 1-113.

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When substituting a for the concentration of $(\text{CH}_3)_3\text{C}-\text{COOH}$ in mol/l. (a_0 is the initial concentration) and b for the concentration of $\text{CH}_2\text{Cl}-\text{C}(\text{CH}_3)_2\text{COOH}$, we obtain the following rate equations:

$$-\frac{da}{dt} = +k_1a[\text{Cl}_2] \quad (3)$$

$$-\frac{db}{dt} = -k_1a[\text{Cl}_2] + k_2b[\text{Cl}_2] \quad (4)$$

When taking $S = k_1/k_2$ as the selectivity of the reaction, and dividing (4) by (3), we obtain:

$$\frac{db}{da} = \frac{1}{S} \cdot \frac{b}{a} - 1 \quad (5)$$

This is a homogeneous differential equation, the solution of which has been given by Jungers¹ as

$$\frac{b}{a_0} = \frac{S}{S-1} \left(\frac{a}{a_0}\right)^{1/S} + \frac{S}{1-S} \left(\frac{a}{a_0}\right) \quad (6)$$

When graphically plotting the function $b/a_0 = f(a/a_0)$ a series of curves is obtained for different values of S . These curves show a maximum value of b/a_0 at the point where as much of b is formed by reaction (1) as disappears by reaction (2).

At this maximum:

$$\frac{db}{dt} = 0 \quad \text{and} \quad k_1a_{\text{max}} = k_2b_{\text{max}} \quad (7)$$

$$S = \frac{k_1}{k_2} = \frac{b_{\text{max}}}{a_{\text{max}}} \quad (8)$$

(a_{max} is the concentration of A at the maximum value of b/a_0)

(b_{max} is the maximum obtainable concentration of B).

B. Results

The chlorination of trimethylacetic acid was carried out in a 1 l. round-bottom Pyrex flask at 60° under external irradiation of a 250 Watt UV source. Chlorine was continuously introduced through a sintered disc at the bottom of the reactor. The escaping hydrochloric acid caused sufficient stirring in order to homogenize the reaction mixture.

At different time intervals a small (1 ml) sample was taken and quantitatively converted to the methyl ester by means of diazomethane.² This was done for facilitating the analysis of the samples, using vapour phase chromatography.

The gas-liquid partition chromatographic analysis was performed on a 2 m long column filled with Apiezon L on Celite at 148° and using He as a carrier gas. The results of this analysis are shown in the Table.

¹ J. C. Jungers, *Cinétique chimique appliquée* p. 173. Technip, Paris (1958).

² H. Schlenk and J. L. Gellerman, *Analyt. Chem.* **32**, 1412 (1960).

TABLE

Sample No.	1	2	3	4	5	6	7	8	9	10
A	66.1*	51.2	42.7	27	21.3	12.1	8.9	4.7	2.2	0.9
B	30.8	43.8	50.0	57.8	57.8	59	55.6	49.1	39.1	27.9
D	1.3	2.9	3.1	6.2	8.6	12	15	19.9	25.3	31.9
E	1.8	2.07	4.4	8.9	12.3	17.9	20.5	26.2	33.4	39.3

* expressed in mole %.

A = trimethylacetic acid

B = monochlorotrimethylacetic acid

D + E: peaks due to two different dichloro derivatives (C) whereas only one was expected.

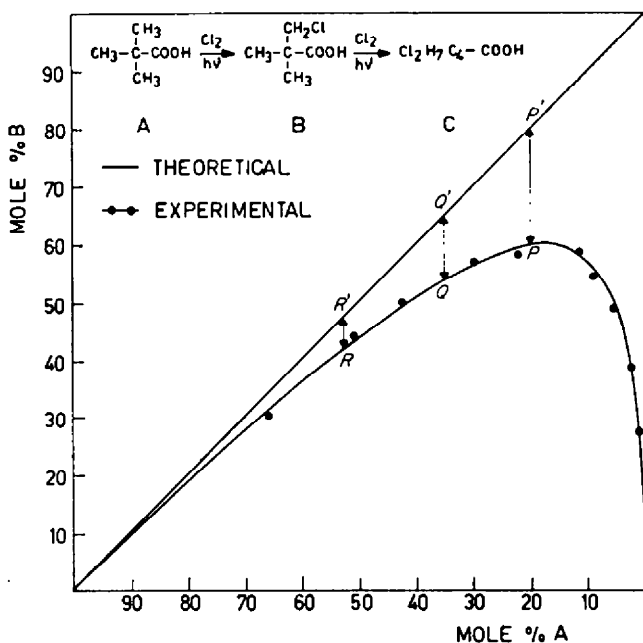


FIG. 1

As predicted by theory, the concentration of monochlorotrimethylacetic acid goes through a maximum, the exact value of which has been graphically determined on a plot of mole % A against mole % B (see Fig.).

It is situated at 60% (mole fraction of $b = 0.6$) when the concentration of residual starting material is 17.5%.

The selectivity S is then

$$S = \frac{0.6}{0.175} = 3.4 = \frac{k_1}{k_2}$$

which means that the first chlorine atom is introduced 3.4 times faster than the second one.

With this value of S the plain (theoretical) curve of the Fig. has been calculated,

using Eq. (6). The experimental points fit in this curve almost perfectly, thus confirming the proposed kinetics.

The diagonal on this Fig. represents the same reaction if

$$\frac{k_1}{k_2} = \infty$$

which means that the total amount of A is converted to B.

The distances PP' , QQ' and RR' between the diagonal and the curve represent the difference between the real yield P , Q , R and that P' , Q' , R' which might be obtained if the intermediate B were the final product.* In this case they are a measure of the loss due to polychlorination.

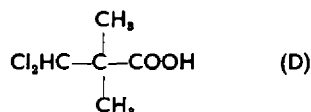
In order to obtain a high yield of monochloro derivative a low conversion chlorination is necessary. Indeed, at a conversion limited to 50% one can calculate the net yield of monochloro derivative to be 92%. We actually found a yield of 90% based on reacted trimethylacetic acid.

The results of the Table also show that a mixture (C) of two dichlorotrimethylacetic acid isomers is formed (D and E).

The ratio of their concentrations seems to be constant for the different samples and equal to 3/4.

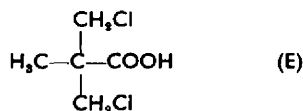
In order to identify both isomers, a larger dichloro fraction of the reaction mixture was esterified and fractionally distilled. Separation was not complete and the two samples could only be purified by preparative gas chromatography.

The IR spectrum of the low boiling compound (D) in the Table shows a splitting of the CH_3 deformation bands in the 7.3μ region, which occurs when two *gem*-methyl groups are present, indicating the formula:

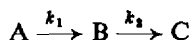


This structure was confirmed by NMR examination. The NMR spectrum comprises a peak at -1.3 ppm with respect to water. This peak may be due to the proton of the CHCl_2 -group.

The NMR spectrum of the product E manifests a peak on $+1.1$ ppm in respect to water. This peak may be due to the 4 protons of the two CH_2Cl -groups. From this it follows that the product E corresponds to the formula:

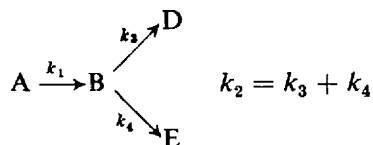


The initially proposed kinetic scheme



* P , Q and R are the actual concentrations of B at different conversions. P' , Q' and R' are the corresponding hypothetical concentrations of B, when B were the final product and C were not formed.

seems to be more complicated therefore and may be represented as:



The ratio k_3/k_4 equals $\frac{3}{2}$ because for parallel reactions of the same order the ratio of the rate constants is equal to the ratio in which the two products are formed.³

Assuming $k_2 = 1$ the following relative rate constants can be calculated

$$k_1 = 3.4 \quad k_2 = 1 \quad k_3 = 0.43 \quad k_4 = 0.57$$

C. Discussion

In order to obtain an idea about the reactivity of the different C—H bonds, the relative rate constants have to be divided by the number of available hydrogens (k_2 has no physical meaning and is omitted)

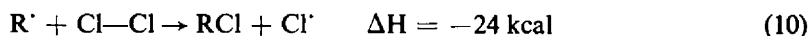
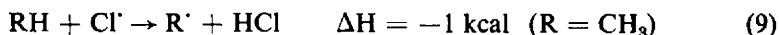
$$k_1' = \frac{3.4 \times 2.65^*}{9} = 1$$

$$k_3' = \frac{0.43 \times 2.65}{2} = 0.57$$

$$k_4' = \frac{0.57 \times 2.65}{6} = 0.25$$

These results, especially the higher rate (k_3') of the attack of chlorine on $-\text{CH}_2\text{Cl}$ *viz.* the rate (k_4') of the attack on $-\text{CH}_3$ seem to stress the importance of radical stabilization in radical chlorination reactions.

Considering the elementary processes by which such reaction proceeds

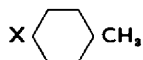


only step "(9)" can determine the rate.⁴

Two factors seem to govern the rate of Eq. 9: the attack of Cl' on the C—H bond, a process which must be strongly influenced by polar factors and the radical stabilization of the incipient free radical R' .

Much attention has been paid recently to the polarity-reactivity relationship in chlorinations.⁵

Indeed, the highly electrophilic chlorine atoms seem to attack preferentially carbon atoms having high electron density electron-withdrawing substituents (COOH , CN , Cl) lowering the reactivity of the α -C—H bonds in RCH_2X and the benzylic C—H in



* 2.65: conversion factor in order to get $k_1' = 1$.

³ J. C. Jungers *Cinetique chimique appliqués* p. 146. Technip, Paris (1958).

⁴ C. Walling, *Free radicals in solution* p. 40. J. Wiley, New York (1957).

^{5a} R. Van Helden and E. C. Kooyman, *Rec. Trav. Chim.* **73**, 269 (1954);

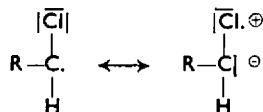
^b C. Walling and B. Miller, *J. Amer. Chem. Soc.* **79**, 4181 (1957);

^c J. Wautier and A. Bruylants, *Bull. Soc. Chim. Belges* **72**, 269 (1963).

Many facts, however, among which the evidence presented in this paper are in apparent contradiction with the above statement. Indeed, in the chlorination of methane,⁶ ethane,⁷ 2-chlorobutane⁸ and trimethylacetic acid, the second chlorine atom preferably attacks the α -carbon atom resulting in *gem*-dichloro compounds.

In these cases the resonance stabilization of the incipient free radical must be of greater importance than the deactivation due to the negative inductive effect of the chlorine substituent already present.

This stabilization can be represented as



where the halogen closely resembles the hybrid structures in halobenzenes.

Although it is impossible to quantitatively assess its magnitude, this resonance stabilization must be quite large, considering the following data.

In the chlorination of α -dimethyl- β -chloropropionic acid, we find a value of 2.28 for the substitution rate of C—H in $-\text{CH}_2\text{Cl}$ vs. 1 in CH_3 . The radical stabilization enhances the rate to a greater extent than the negative inductive effect of Cl reduces it. In the chlorination of toluene and benzylchloride, however,⁹ the second chlorine is introduced about eleven times more slowly than the first, giving a value per C—H bond of 1 to 7. In this case the benzylic resonance stabilization largely outweighs the stabilization due to chlorine and the relative reactivity in CH_3 , and CH_2Cl is governed only by the deactivating influence of the electron-withdrawing chlorine.

Suppressing in this way the mesomeric effect of the halogen, the relative reactivity in CH_2Cl to CH_3 is reduced from 2.28/1 to 1/7.

The reactivity of different C—H bonds in a halogenated molecule toward radical halogenation seems therefore to be governed by a delicate balance between polar effects, due to the $-I$ effect, and resonance stabilization of the free radical, owing to the $+M$ effect of the halogen substituent.¹⁰

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⁶ H. O. Pritchard, J. B. Pike and A. F. Trotman-Dickenson, *J. Amer. Chem. Soc.* **77**, 2629 (1955).

⁷ W. E. Vaughan and F. F. Rust, *J. Org. Chem.* **6**, 479 (1941).

⁸ P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.* 3520 (1961).

⁹ G. Benoy and J. C. Jungers, *Bull. Soc. Chim., Belges* **65**, 769 (1956).

¹⁰ See also J. Hine, *Physical Organic Chemistry* (2nd Edition) p. 459. McGraw-Hill, New York (1962).