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KINETICS OF OXIDATION OF SUBSTITUTED TOLUENES WITH CHROMYL CHLORIDE

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Abstract—The kinetics of oxidation of substituted toluenes with chromyl chloride in carbon disulphide solution has been studied. The value obtained for the Hammett reaction constant, ρ, is $-2{\cdot}20 \pm 0{\cdot}08$. This is consistent with the theory that reaction involves a cyclic transition state.

IT HAS been known[1] that chromyl chloride reacts with toluene to yield a brown, amorphous solid the composition of which corresponds to $PhCH_3{\cdot}2CrO_2Cl_2$ and which hydrolyses to benzaldehyde. Recently,[2] we have presented evidence directly related to the structure of the adduct. However, although kinetic studies[3] have shown that reaction is first order with respect to each of the reactants, whilst isotopic tracer studies[4,5] have shown that carbon–hydrogen bond cleavage occurs in the rate determining step, the mode of cleavage of the carbon–hydrogen bond has not been clarified. The mechanism of the related oxidation of diphenylmethane has been discussed by Nenitzescu[6] and Wiberg,[7] the former favouring a carbonium ion mechanism and the latter a free radical mechanism. We have studied the effects of substituents on the rates of reaction of a series of substituted toluenes with chromyl chloride in order to obtain evidence relating to the rate determining step.

Our results show that nuclear substituted toluenes exhibit good second-order kinetics on the assumption that Eqs. (1) and (2) apply.

$$XC_6H_4CH_3 + CrO_2Cl_2 \xrightarrow{\text{slow}} XC_6H_4CH_3/CrO_2Cl_2 \qquad (1)$$

$$XC_6H_4CH_3/CrO_2Cl_2 + CrO_2Cl_2 \xrightarrow{\text{fast}} XC_6H_4CH_3/2CrO_2Cl_2 \qquad (2)$$

Thus, second-order rate constants were obtained by calculating the slope of the line of $\ln B(2A - x)/2A(B - x)$ against time, where:

A = initial concentration of the toluene

B = initial concentration of chromyl chloride

$(B - x)$ = concentration of chromyl chloride at time t.

The "least squares" rate constants thus obtained are given in Table 1.

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[1] W. H. Hartford and M. Darrin, *Chem. Rev.* **58**, 1 (1958).

[2] H. C. Duffin and R. B. Tucker, *Chem. & Ind.* **29**, 1262 (1966).

[3] R. A. Stairs and J. W. Burns, *Canad. J. Chem.* **39**, 960 (1961).

[4] O. H. Wheeler, *Canad. J. Chem.* **42**, 706 (1964).

[5] I. P. Gragerev and M. P. Ponomarchuk, *Zh. Obshch. Khim.* **32**, 3568 (1962).

[6] I. Necsoiu, A. T. Balaban, I. Pascaru, E. Sliam, M. Elian and C. D. Nenitzescu, *Tetrahedron* **19**, 1133 (1963).

[7] K. B. Wiberg and R. Eisenthal, *Tetrahedron* **20**, 1151 (1964).

The rate constant for the reaction of benzyl chloride, which forms only a 1:1 adduct,[1] was calculated on the assumption that the equivalent of Eq. (1) only applies. Again, good second-order kinetics were observed.

Our value of the rate constant for the oxidation of toluene in carbon tetrachloride is 22% lower than that of Stairs and Burns.[3] However, this discrepancy is easily accounted for since Stairs and Burns used residual oxidizing power as their criterion for extent of reaction. We have found that residual oxidizing power is variable and usually less than theoretical.[2] Thus, rate constants based on this property would be expected to be high.

In agreement with the oxidation of substituted diphenylmethanes by chromic acid[8] electron withdrawing substituents are seen to slow the reaction whereas electron releasing substituents have the opposite effect. The "least squares" value of the Hammett reaction constant, ρ, evaluated from the kinetic data is $-2{\cdot}28 \pm 0{\cdot}08(0)$. The corresponding value for ρ^+ is $-2{\cdot}20 \pm 0{\cdot}07(9)$. The values of σ and σ^+ employed in the calculations were those given by Brown and Okamoto.[9] The available data do not permit a choice to be made between ρ and ρ^+ values. Unfortunately, methoxy substituted toluenes could not be included since the methoxy group facilitates attack on the aromatic nucleus.[10]

The value obtained for ρ indicates that carbonium ions cannot be produced in the rate determining step, for, if they were, a value between -3 and -5 would be expected.[8]

Conversely, values of ρ^+ for hydrogen atom abstractions from the side chain of substituted toluenes normally lie between $-0{\cdot}75$ and $-1{\cdot}5$.[11] Wilberg has likened oxidation by chromic acid to hydrogen atom abstraction by bromine atoms since the two reactions exhibit similar selectivities.[7] Further, Wiberg and Evans[8] obtained the value $-1{\cdot}17$ for chromic acid oxidation of diphenylmethanes and compared this with the value $-1{\cdot}12$ calculated from the results for the analogous oxidation of toluenes.[12] The value reported for the bromination of substituted toluenes is $-1{\cdot}05$.[13]

In bromination, however, radical stabilization appears to be of greater importance than the electronegativity of the bromine atom since hydrogen attached to carbon directly bonded to halogen is more readily substituted than if the halogen substituent were absent.[13] In contrast, it is well known[1] that benzyl chloride is less readily oxidized than toluene by chromyl chloride. We find that the ratio of the rate constants is approximately 1:5 (Table 1). Thus, in the case of oxidations by chromyl chloride the electronegativity of the attacking species appears to be dominant. It is probably better, therefore, to compare chromyl chloride oxidations with hydrogen atom abstraction by trichloromethyl radicals. Evidence[14] indicates that the methyl group of α-bromo-*p*-xylene is more readily attacked by trichloromethyl radicals than the bromomethyl group. The value of ρ^+ reported for abstraction of benzylic hydrogen atoms by trichloromethyl radicals is $-1{\cdot}46$.[14] However, although this is appreciably

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[8] K. B. Wiberg and R. J. Evans, *Tetrahedron* **8**, 313 (1960).

[9] H. C. Brown and Y. Okamoto, *J. Org. Chem.* **22**, 485 (1957).

[10] J. S. Strickson and C. A. Brooks, Private communication.

[11] H. H. Jaffe, *Chem. Rev.* **53**, 191 (1953).

[12] Y. Ogata, A. Fukui and S. Yuguchi, *J. Am. Chem. Soc.* **74**, 2707 (1952).

[13] J. M. Tedder, *Quart Rev.* **14**, 343 (1960).

[14] E. S. Huyser, *J. Am. Chem. Soc.* **82**, 391 (1960).

closer to our value of $-2{\cdot}20$ than is the value for bromination, the difference is probably still too large to be explained solely in terms of difference in electronegativities.

Before free radical formation is ruled out altogether it is necessary to consider the possibility of pre-transition state complex formation since this could lead to a significant increase in the value of ρ.[15] Indeed, Wheeler has suggested that π complex formation may occur before hydrogen abstraction.[16] If this were the case it would be reasonable to expect large solvent effects in changing from aliphatic to aromatic solvents. We have detected no significant difference in reaction rate for oxidation of toluene in carbon disulphide, carbon tetrachloride and benzene. The relevant rate constants are shown in Table 1. The observed changes in rate are appreciably less than those noted by Stairs for a series of halogenated alkanes.[17]

It seems probable, therefore, that the reaction of toluene with chromyl chloride involves a cyclic transition state of the type considered by Wilberg,[18] and believed by him to offer a possible explanation both for oxidations by chromic acid and by chromyl chloride. The value obtained for ρ is then explicable in that a bond is being formed between benzylic carbon and oxygen whilst the carbon–hydrogen bond is being broken, as shown in Fig. 1.

Apart from its non-linearity, this transition state may be compared with that for the bimolecular solvolysis of benzyl halides. Thus, hydride ion abstraction may be regarded as replacing halide ion expulsion whilst, in each case, a bond is being formed from carbon to oxygen. The value of ρ^+ for solvolysis of benzyl halides in 48% aqueous ethanol is reported as $-2{\cdot}18$.[15] Whilst it is recognised that significantly different solvents are employed in the two reactions, the similarity in ρ values is noteworthy.

We therefore conclude that the kinetics of oxidation of substituted toluenes are best explained on the assumption that the reaction involves a cyclic transition state.

Whilst writing this paper we have become aware of a recent publication in which a transition state identical to the one we favour is postulated for the chromyl chloride oxidation of phenylmethanes.[19] However, the writers draw their conclusions from a consideration of non kinetic evidence. Nenitzescu *et al.*[19] have drawn analogy with heterolytic mechanisms, as we have. However, there is no obvious reason why unpaired electron shifts should not occur in the proposed cyclic transition state since the degree of charge separation would be similar. Our earlier work[2] has shown that the toluene adduct consists of benzaldehyde co-ordinated with chromium compounds in oxidation states intermediate between III and VI. Thus a second C—H bond has been broken at the adduct stage. It is unlikely that this second step involves hydride ion abstraction since the carbon is now bonded to a strongly electronegative group. It seems much more plausible that the organic group attached to chromium is an incipient alkoxy radical which readily loses a hydrogen atom to a second molecule of chromyl chloride. Further, no attempt has been made to explain why, if chromyl

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[15] K. B. Wiberg, *Physical Organic Chemistry* p. 407. Wiley (1963).

[16] O. H. Wheeler, *Canad. J. Chem.* **36**, 667 (1958).

[17] R. A. Stairs, *Canad. J. Chem.* **40**, 1656 (1962).

[18] K. B. Wiberg, *Oxidations in Organic Chemistry* Part A; p. 69. Academic Press, New York (1965).

[19] I. Necsoiu, V. Przemetchi, A. Ghenciulescu, C. N. Rentea and C. D. Nenitzescu, *Tetrahedron* **22**, 3037 (1966).

chloride is the powerful electrophile suggested by Nenitzescu and co-workers, the aromatic ring is so unreactive.

Thus, although it seems essentially proven that a cyclic transition state is involved in the rate determining step it is certainly not clear whether the role of chromyl chloride is one of an electrophile or a free radical.

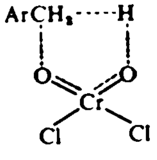

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TABLE 1. SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF SUBSTITUTED TOLUENES WITH CHROMYL CHLORIDE

Hydrocarbon	Concentration (mole/litre)	Solvent	Rate constant (l/mole sec)
Toluene	0·2175	CS_2	$4·67 \pm 0·13 \times 10^{-4}$
p-Me_3C—	0·2175	CS_2	$1·46 \pm 0·03 \times 10^{-3}$
p-Cl—	0·2175	CS_2	$2·24 \pm 0·04 \times 10^{-4}$
m-Cl—	0·2175	CS_2	$7·23 \pm 0·02 \times 10^{-5}$
p-Br—	0·2175	CS_2	$1·84 \pm 0·05 \times 10^{-4}$
p-I—	0·2175	CS_2	$2·05 \pm 0·03 \times 10^{-4}$
p-NO_2—	0·2175	CS_2	$1·21 \pm 0·04 \times 10^{-6}$
m-NO_2—	0·2175	CS_2	$9·20 \pm 0·33 \times 10^{-6}$
p-Me—	0·1088	CS_2	$1·59 \pm 0·04 \times 10^{-3}$
m-Me—	0·1088	CS_2	$6·54 \pm 0·07 \times 10^{-4}$
Toluene	0·2175	CCl_4	$4·38 \pm 0·09 \times 10^{-4}$
p-NO_2—	0·2175	CCl_4	$1·27 \pm 0·02 \times 10^{-6}$
Toluene	0·2175	C_6H_6	$7·13 \pm 0·32 \times 10^{-4}$
Benzyl Chloride	0·2175	CS_2	$9·56 \pm 0·13 \times 10^{-6}$

All reactions conducted at 40° with a chromyl chloride conc. of 0·1234 mole/litre. All rate constants are the average of two runs.

EXPERIMENTAL

Materials. All materials were commercially available. Solvents were dried over $CaCl_2$ and distilled, the fractions with the literature b.ps being collected. The substituted toluenes were appropriately dried and used without further purification. The CrO_2Cl_2 was subjected to two room temp vac. distillations immediately before use.

Kinetic measurements. Kinetic runs were followed by determining the rate of production of adduct. Samples (15 ml) of reaction mixture, appropriately thermostatted, were pipetted into tared centrifuge tubes fitted with ground glass caps. The filled tubes were inserted into waterproof polythene bags and totally immersed in the thermostat. At appropriate intervals tubes were withdrawn, centrifuged and the solvent decanted. The adduct samples were twice washed with fresh solvent before vac. drying and weighing *in situ*.