

# KINETICS OF OXIDATION OF SUBSTITUTED TOLUENES WITH CHROMYL CHLORIDE—II<sup>1</sup>

## EFFECT OF TEMPERATURE

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**Abstract**—The value  $-2.32 \pm 0.10$  has been obtained for the Hammett reaction constant  $\rho^+$  for oxidation of substituted toluenes with chromyl chloride at 25°. This, together with the value  $-2.20 \pm 0.08$  obtained previously<sup>1</sup> at 40° yields a value  $730 \pm 140^\circ\text{K}$  for the isokinetic temperature  $\beta$ , a linear relationship being found to exist between  $\Delta H^*$  and  $\Delta S^*$

THE oxidation of substituted toluenes by chromyl chloride at 40° has recently been reported.<sup>1</sup> The value of the Hammett reaction constant  $\rho^+$  obtained from the data was  $-2.20 \pm 0.08$ . In drawing conclusions concerning the mechanism of the reaction it was tacitly assumed that variation of the free energy of activation with substituent ( $\delta\Delta G^*/\delta\sigma$ , where  $\sigma$  is the Hammett substituent constant) was approximately independent of temperature. Thus, it was assumed that the entropy of activation ( $\Delta S^*$ ) for the reaction was independent of substituent. In these circumstances  $\rho_1/\rho_2 = T_2/T_1$  so that variation of  $\rho$  with temperature is small.<sup>2</sup> Then, the calculated value for  $\rho^+$  at 25° is  $-2.31$ . Comparison with other reactions was, therefore, assumed to be justified and it was concluded that the rate determining step involved a cyclic transition state.

Leffler<sup>3</sup> has shown that  $\Delta H^*$  and  $\Delta S^*$  can be linearly related by the equation:

so that

$$\Delta H^* = \Delta H_0^* + \beta\Delta S^*$$

$$\Delta G^* = \Delta H_0^* - (T - \beta)\Delta S^*$$

Then if  $\beta$ , termed the isokinetic temperature, is within the experimentally accessible temperature range  $\rho$  can change sign with consequent ambiguity in interpretation in terms of reaction mechanism.

Stairs has found  $\rho^+$  for oxidation of substituted toluenes with chromyl chloride to vary from  $-3.94$  at 1° to  $-1.58$  at 40°, the value of  $\beta$  being only 343°K.<sup>4</sup> This value for  $\beta$  is unexpectedly low, Exner having stated<sup>5</sup> that it can be assumed that the isokinetic temperature is always far from experimental temperatures. However, Stairs followed the reaction by observing the variation in total residual oxidizing power. We believe this technique to be unreliable since oxidizing power can be lost in side reactions. Examples of such side reactions are the formation of chlorinated products and the oxidation of aldehyde present in the adduct<sup>6</sup> to the carboxylic acid.<sup>7</sup>

In view of these facts we have examined the kinetics of the reaction at a second temperature (25°) using our technique of observing the rate of formation of adduct. As at 40°, good second order kinetics were observed in all cases. The rate constants,

given in Table 1, were calculated as described previously.<sup>1</sup> As before, the values for methyl substituted toluenes have been halved for statistical reasons. The value of  $\rho^+$  calculated from these results is  $-2.32 \pm 0.10$ , in good agreement with the result predicted above.

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

Substituent	Concentration (mole/litre)	Temperature (°C)	Rate constant (1/mole sec)
H	0.2175	25	$1.31 \pm 0.04 \times 10^{-4}$
<i>p</i> -Me	0.1088	25	$5.24 \pm 0.22 \times 10^{-4}$
<i>m</i> -Me	0.1088	25	$2.30 \pm 0.06 \times 10^{-4}$
<i>p</i> -Me <sub>3</sub> C	0.2175	25	$4.47 \pm 0.13 \times 10^{-4}$
<i>m</i> -Cl	0.2175	25	$1.52 \pm 0.04 \times 10^{-5}$
<i>p</i> -Cl	0.2175	25	$5.27 \pm 0.23 \times 10^{-5}$
<i>p</i> -I	0.2175	25	$6.43 \pm 0.19 \times 10^{-5}$
<i>p</i> -Br	0.2175	25	$4.86 \pm 0.08 \times 10^{-5}$
<i>p</i> -NO <sub>2</sub>	0.2175	25	$2.52 \pm 0.04 \times 10^{-6}$
<i>m</i> -NO <sub>2</sub>	0.2175	25	$1.97 \pm 0.08 \times 10^{-6}$
<i>m</i> -Br	0.2175	25	$1.48 \pm 0.02 \times 10^{-5}$
<i>m</i> -I	0.2175	25	$1.71 \pm 0.02 \times 10^{-5}$
<i>m</i> -Br	0.2175	40	$6.31 \pm 0.13 \times 10^{-5}$
<i>m</i> -I	0.2175	40	$7.33 \pm 0.13 \times 10^{-5}$

All reactions conducted in CS<sub>2</sub> solution with a chromyl chloride concentration of 0.1234 mole/l. All rate constants are the average of two runs.

It has been shown<sup>5</sup> that  $\beta$  can be calculated from the slope,  $\lambda$ , of the plot of  $\log k$  at  $T_1$  against  $\log k$  at  $T_2$  where  $k$  is the rate constant, using the relationship:

$$\beta = T_2 \frac{T_1 \lambda - T_1}{T_1 \lambda - T_2}$$

From our results, shown in Fig. 1,  $\lambda = 0.915 \pm 0.012$  so that  $\beta = 730 \pm 140^\circ\text{K}$ . Since  $T_2/T_1 = 0.95$ , these results put the reaction in Exner's category<sup>5</sup> 3a, namely the most common category. The results also clearly indicate that the conclusions given in our previous paper are not invalidated by variation of  $\rho$  with temperature.

Bearing in mind the observations of Exner<sup>5</sup> and Leffler<sup>8</sup> it is useful to examine the values of  $\Delta G^*$ ,  $\Delta H^*$ , and  $\Delta S^*$  calculated from the above data. The values are given in Table 2. Further,  $\Delta H^*$  is plotted against  $\Delta S^*$  in Fig. 2. Average variation of  $\Delta H^*$  with  $\Delta S^*$  is indicated by the full line of slope  $\beta$ . Variation of  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  with  $\sigma$  are given by:

$$(\delta\Delta G^*/\delta\sigma)_{298} = 3.15 \pm 0.12 \text{ kcal};$$

$$(\delta\Delta G^*/\delta\sigma)_{313} = 3.01 \pm 0.12 \text{ kcal}$$

$$\delta\Delta H^*/\delta\sigma = 6.0 \pm 0.9 \text{ kcal}$$

$$\delta\Delta S^*/\delta\sigma = 9.3 \pm 3.2 \text{ cal/deg.}$$

TABLE 2. THERMODYNAMIC CONSTANTS FOR THE OXIDATION OF SUBSTITUTED TOLUENES WITH CHROMYL CHLORIDE

Substituent	$\Delta G_{313}^*$ (kcal/mole)	$\Delta G_{298}^*$ (kcal/mole)	$\Delta H^*$ (kcal/mole)	$\Delta S^*$ (cal/deg/mole)
H	23.12	22.74	15.1	-25.6
<i>p</i> -Me	22.36	21.92	13.1	-29.5
<i>m</i> -Me	22.95	22.40	12.3	-33.8
<i>p</i> -Me <sub>3</sub> C	22.42	22.01	14.0	-26.8
<i>m</i> -Cl	24.28	24.01	18.7	-17.8
<i>p</i> -Cl	23.58	23.27	17.3	-20.1
<i>p</i> -I	23.92	23.16	13.7	-31.6
<i>p</i> -Br	23.70	23.33	15.9	-25.1
<i>p</i> -NO <sub>2</sub>	25.40	25.07	18.8	-21.0
<i>m</i> -NO <sub>2</sub>	25.57	25.23	18.5	-22.7
<i>m</i> -Br	24.37	24.05	17.3	-22.6
<i>m</i> -I	24.28	23.95	17.4	-22.1

Maximum probable errors are:  $\Delta G^*$ ,  $\pm 0.03$ ;  $\Delta H^*$ ,  $\pm 1.0$ ;  $\Delta S^*$ ,  $\pm 3.0$ .

The values for  $\delta\Delta G^*/\delta\sigma$ , which are effectively indistinguishable, emphasize the validity of our earlier assumption that conclusions could be drawn from the value of  $\delta\Delta G^*/\delta\sigma$  ( $= 2.303RT\rho$ ) at one temperature only.

Stairs found  $\delta\Delta S^*/\delta\sigma = 72 \pm 10$  cal/deg and, from this unusually high value concluded that  $\pi$  complex formation must precede reaction. Our value is seen to be normal thus supporting our previous conclusion, based on an examination of the effect of a change from aliphatic to aromatic solvents, that  $\pi$  complex formation does not occur.<sup>1</sup> We recognize, however, that some sort of loose association of the type postulated by Stairs<sup>4</sup> must occur.

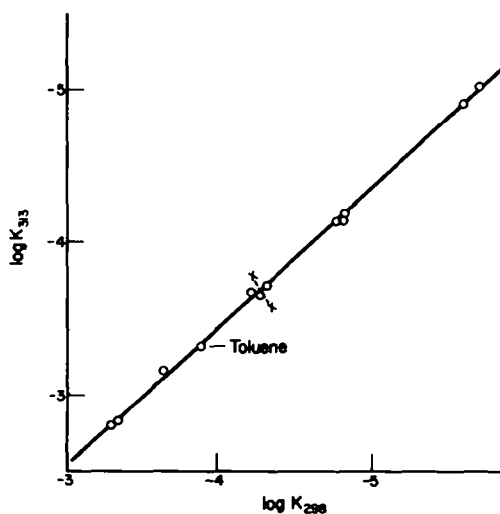


FIG. 1 Plot of rate constants at 313°K against rate constants at 298°K for reaction of substituted toluenes with chromyl chloride.

An examination of Fig. 2 reveals apparent relationships of the type recognized by Brown.<sup>9</sup> In particular, values for p-halogen substituted species fall, in a logical sequence, on a line for which  $\beta$  equals the average temperature of the determinations (broken line XX). Exner<sup>5</sup> has shown that it is dangerous to draw conclusions from such apparent relationships since errors are seriously distorted along lines with  $\beta = T$ . He prefers the presentation of data as in Fig. 1 so that no such distortion of errors occurs. When the broken line from Fig. 2 is mapped back onto Fig. 1 (broken line XX)

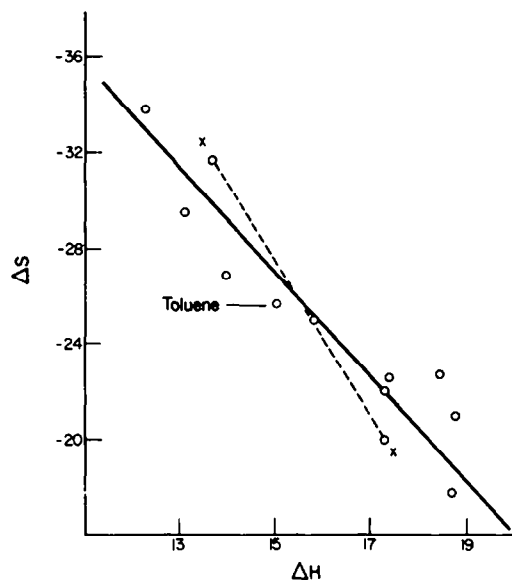


FIG. 2 Plot of entropy of activation (cal/deg/mole) against enthalpy of activation (kcal/mole) for reaction of substituted toluenes with chromyl chloride.

in the manner recommended by Exner the lack of a genuine, linear relationship becomes evident.

We conclude therefore that the reaction of substituted toluenes with chromyl chloride is normal and that a linear relationship exists between  $\Delta H^*$  and  $\Delta S^*$  given by:

$$\Delta H^* = \Delta H_0^* + 730\Delta S^*$$

We further conclude that no subsidiary relationships of the type recognized by Brown exist.

#### EXPERIMENTAL

The reactions were conducted as described previously<sup>1</sup> the use of tared centrifuge tubes permitting accurate weighing of precipitated solid at appropriate intervals.

#### REFERENCES

- <sup>1</sup> H. C. Duffin and R. B. Tucker, *Tetrahedron* **23**, 2803 (1967).
- <sup>2</sup> P. R. Wells, *Chem. Rev.* **63**, 171 (1963).
- <sup>3</sup> J. E. Leffler, *J. Org. Chem.* **20**, 1202 (1955).

- <sup>4</sup> R. A. Stairs, *Canad. J. Chem.* **42**, 550 (1964).
- <sup>5</sup> O. Exner, *Coll. Czech. Chem. Commun.* **29**, 1094 (1964).
- <sup>6</sup> H. C. Duffin and R. B. Tucker, *Chem. & Ind.* **29**, 1262 (1966).
- <sup>7</sup> W. H. Hartford and M. Darrin, *Chem. Rev.* **58**, 1 (1958).
- <sup>8</sup> J. E. Leffler, *J. Org. Chem.* **31**, 533 (1966).
- <sup>9</sup> R. F. Brown, and H. C. Newsom, *J. Org. Chem.* **27**, 3010 (1962).