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AROMATIC NITRATION IN CARBON TETRACHLORIDE - A NEGATIVE TEMPERATURE COEFFICIENT

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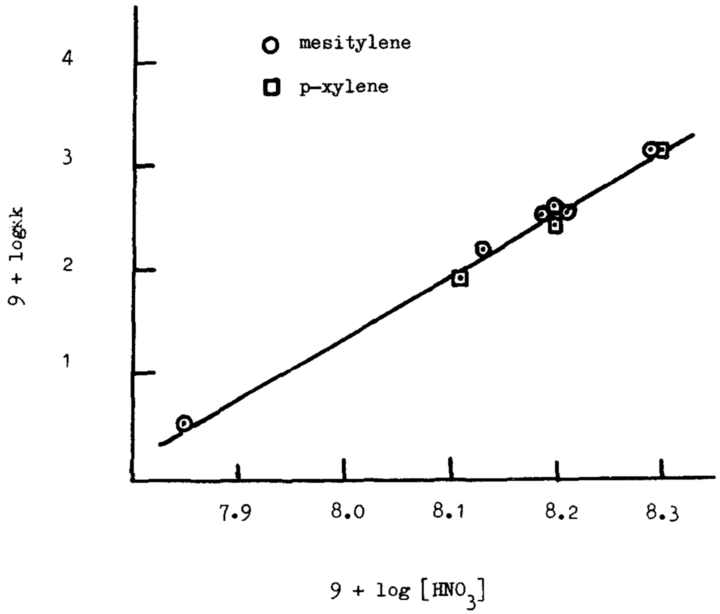
Kinetic studies we have made on the reaction of aromatic substrates with anhydrous nitric acid in carbon tetrachloride show that the rates of nitration of benzene, toluene, p-xylene and mesitylene are very similar (see Table 1) and are all zeroth order in the aromatic compound. The rate dependence on the nitric acid concentration (always in at least a 10:1 excess over the aromatic substrate) indicates an order of 6 in the two cases studied in detail - mesitylene and p-xylene (see Fig.). Similar but much less precisely established high orders in nitric acid have been reported for the nitration of benzene by nitric acid in nitromethane (1), of p-chloroanisole by dinitrogen tetroxide and nitric acid in acetic acid (2) and of halogenated benzenes by dinitrogen pentoxide and nitric acid in carbon tetrachloride (3).

The encounter rate interpretation (4) i.e. that reaction occurs at every collision between the substrate and a highly active nitrating species such as the nitromium ion, NO_2^+, present in extremely low concentration has been recently proposed for nitration in aqueous sulphuric acid (5), in which several aromatic hydrocarbons were found to nitrate at the same rate. Reactions with a high order in nitric acid, however, suggest that desolvation of a solvated ionic or polar entity may be the rate limiting step. A highly solvated reactant is unlikely to form a -complex (or -complex) with equal facility with all four of the substrates indicated in Table 1 and the similarity in rate which has been found may therefore arise from the operation of the same desolvation mechanism in all cases to produce a highly reactive nitrating entity. An aggregate of six nitric acid molecules may be the source of a nitrating agent such as the nitric acidium ion or nitrogen pentoxide either of which would require solvation to produce a nitronium ion.

It is reasonable to expect that reaction via a highly solvated species would show a marked temperature effect since solvation in this system must be very sensitive to change of

FIG.



temperature. Rates of nitration of mesitylene were therefore measured at 0° and 40° and they reveal a substantial increase in rate at the lower temperature and a similar decrease at the higher temperature (Table 2). The order in nitric acid is approximately at 6 at both temperatures.

Conductivity measurements on anhydrous nitric acid have shown that self dissociation of the acid as represented with equation (1)

$$2HNO_3 \rightleftharpoons NO_2^{\oplus} + NO_3^{\ominus} + H_2O \qquad (1)$$

also increases with lowering of temperature (6). If the same process occurs in carbon tetrachloride solution it must be greatly dependent on solvation of the ionic species by undissociated nitric acid molecules. Increase of temperature would clearly impede the solvation and reduce the concentration of nitronium ion and therefore the rate of reaction. The equilibrium constant, K, of reaction (1) was reported to increase by a factor of ca. 1.8 for a decrease in temperature of 10° corresponding approximately to a factor of ca. 10 for a 40° change in temperature. Although the effect of carbon tetrachloride on (1) is difficult to interpret, the rate of nitration for a 40° change in temperature increases by such a large factor viz. 300 times (see Table 2) that it is unlikely to arise only through a change in K for reaction (1).

TABLE 1

Rates of nitration with nitric acid (ca. 0.15M) at 25°.

substrate (ca.6 x 10^{-3}M)	benzene	toluene	p-xylene	mesitylene
10^7k(mole.litre^{-1}sec.$^{-1}$)	2.65	3.20	2.79	3.14

TABLE 2

Rates of nitration of mesitylene with nitric acid at 0° and 40°.

	Mesitylene 10^3M	Nitric Acid 10M	10^7k mole sec.$^{-1}$	10^4k/$[HNO_3]^6$
40°	8.74	1.319	0.435	8.3
	8.74	1.99	5.70	9.2
0°	12.4	1.17	78.4	3,060
	12.4	.691	2.77	2,530

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