

Catalysis by NO^+ of the Reaction of 1,2,3-Trimethoxy-5-nitrobenzene with Nitric Acid. Evidence for a Limiting Kinetic Form Zeroth-order in Nitric Acid

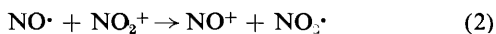
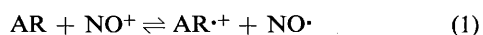
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The reaction in sulphuric acid of 1,2,3-trimethoxy-5-nitrobenzene with mixtures of nitrous and nitric acids occurs under conditions in which reactions with either acid alone are negligibly slow, and it has the limiting kinetic form zeroth-order in nitric acid which is consistent with the electron-transfer mechanism for NO^+ -catalysis proposed by Giffney and Ridd.

Ross, Hum, and Blucher have shown¹ that catalysis by nitrous acid of the nitration of phenol involves a mechanism other than nitrosation plus oxidation. They suggested the possibility of an electron transfer role for the catalyst in a mechanism [*e.g.* equations (1)–(3); AR = aromatic compound] of the



type first substantiated² by Giffney, Ridd, and coworkers in studies of the nitration of *N,N*-dimethylanilinium ions. This raises the question of whether such a mechanism is more general in aromatic nitration than has hitherto been perceived. Our results suggest that this may be so.

Supporting such a mechanism for *N,N*-dimethylanilinium ions was^{2a} a zeroth order dependence [equation (4)] on nitric

$$\text{Rate} = k[\text{AR}][\text{NO}^+] \quad (4)$$

acid at high concentrations, *i.e.* those concentrations sufficient to trap [*e.g.* equation (2)] all NO formed in equation (1), which then is no longer reversed. We have now established the same limiting kinetic form for 1,2,3-trimethoxy-5-nitrobenzene with mixtures of nitrous and nitric acid under conditions (Figure 1) such that reaction with either acid alone is negligibly slow. The limiting rate coefficients ($k_{\text{obs}}/[\text{NO}^+]$) are approximately the same (*ca.* $2.8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) in 62.1% and 70.5% H_2SO_4 . This is consistent with the reaction being rate-limited at these different acidities by the same step(s), *e.g.* the formation of $\text{NO}\cdot$ [equation (1)], and it excludes

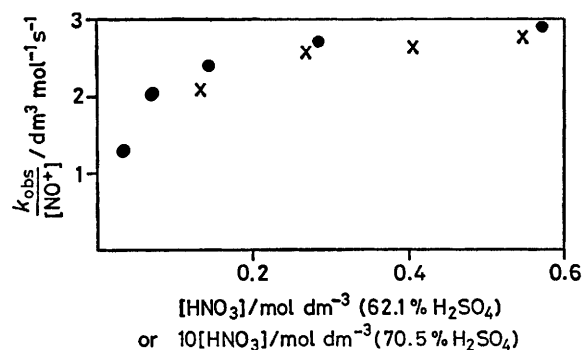


Figure 1. $k_{\text{obs}}/[\text{NO}^+]$ at 25 °C for 1,2,3-trimethoxy-5-nitrobenzene (*ca.* $2.5 \times 10^{-4} \text{ mol l}^{-1}$) in 70.5% (●) and 62.1% (×) H_2SO_4 . Data cover a 2- to 4-fold variation in $[\text{NO}^+]$ ($\leq 10^{-2} \text{ mol l}^{-1}$). Reactions become slower as $[\text{HNO}_3]$ is further decreased but do not remain properly first-order in 1,2,3-trimethoxy-5-nitrobenzene.

catalysis by HNO_3 rather than NO^+ . The value of the rate coefficient is many (*ca.* 10^8) times smaller than that for a diffusion-controlled encounter,³ which is consistent⁴ with an endergonic electron transfer in equation (1). The nitric acid concentration at which the zeroth-order kinetics are attained is *ca.* 10 times larger in 62.1% than in 70.5% H_2SO_4 . Since it can be estimated³ that the fraction of nitric acid present as NO_2^+ decreases by a factor of $> 10^3$ between 70.5% and

62.1% H_2SO_4 , equation (2) with free NO_2^+ cannot be the only reaction by which the products of equation (1) react further with nitric acid. These kinetic characteristics of the reaction are thus wholly analogous to those of the reaction of the *N,N*-dimethylanilinium cation.^{2a} Likewise, reactions without, or with low concentrations of, added NO^+ were autocatalytic; repetitive scans revealed a product with the absorbance characteristics of NO^+ which could be removed by reaction with hydrazine.

We are pursuing the possibility that a transient red species also observed is the cation radical or some other intermediate on the reaction pathway.

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References

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