Tetrahedron Letters No. 1, pp 17 - 18, 1972. Pergamon Press. Printed in Great Britain.

THE NITRATION OF DIMETHYLPHENYLSULPHONIUM METHYL SULPHATE IN CONCENTRATED SULPHURIC ACID

N.C.Marziano, E.Maccarone and R.C.Passerini
Facoltà di Chimica Industriale Università,
Dorsoduro 1686 - 30123 Venezia - Italy.

(Received in UK 9 August 1971; accepted for publication 1 December 1971)

The results obtained in the nitration of diphenylsulphoxide in concentrated sulphuric acid, support the hypothesis that reaction occurs in part through the neutral molecule and in part through the conjugated acid (1). The evidence for this mechanistic distinction comes from the comparison with aromatic substrates possessing an amino group as an ammonium pole.

This comparison may appear open to criticism. Therefore, in order to extend the kinetic analysis of the nitration of sulphoxides we have studied the kinetics of the nitration of dimethylphenylsulphonium methyl sulphate.

Observed second-order rate constants in concentrated sulphuric acid are reported in table 1; the slopes of the rate profile below and above 90% sulphuric acid are: 0,284 and -0,047. The Arrhenius parameters calculated at 96,2% of sulphuric acid are: E_a=12,9 Kcal mol^{-1}; $\log_{10}A$=6,67 s^{-1} and $\Delta S^{\ddagger}$=-28,0 cal.mol.$^{-1}$ K^{-1}.

We have also calculated the reactivity of the substrate in order to relate the sulphur substituent effect to other positive poles (2).

The isomeric composition obtained in the nitration of the sulphonium salt ($\sim 10^{-3}$M.) with nitric acid ($\sim 10^{-2}$M.) in sulphuric acid at 25°C. for 24 hrs gives the following results: *ortho*=2,18%; *meta*=93,87% and *para*=3,95%. These values are the average of different runs carried out over the range of sulphuric acid (85-96%). The isomeric ratio, independent of the acid concentration, was obtained by g.l.c. analysis (3) of the products, after conversion of the *ortho*- and *para*- nitrophenylsulponium ion to *ortho*- and *para*-nitroanisoles (3,4) and *meta* isomer to *meta*-nitrothioanisole (3). Our results show somewhat less *ortho*- and *para*-substitution than recently reported (3).

The reactivity of substrate relative to benzene (5) calculated by a step-wise comparison from the slope at lower aciditied is $1,06\cdot10^{-9}$. The value $3,98 \times 10^{-9}$ is obtained at 98,7% of sulphuric acid from the relative rate with respect to phenyltrimethyl ammonium ion (2). The latter gives the following partial factors: $f_{\underline{o}} = 2,60\cdot10^{-10}$; $f_{\underline{m}} = 1,12\cdot10^{-8}$ and $f_{\underline{p}} = 9,44\cdot10^{-10}$.

The results support the hypothesis of an electrostatic interaction of the positive charge increased by the partecipation of "3d" orbital in the valence state of the sulphur (6) for the dimethylsulphonium group. Evidence for π (d-p) overlap derives from the smaller percentages of the *para* position compared to that of the nitrogen compounds. A similar trend is observed in the nitration of aromatic substrates carrying other poles with vacant "d" orbitals in the valence shell (2). Relative to phenyltrimethylammonium ion the f_m value is lower by a factor of ca.8, the f_p by a factor of ca.25.

Other evidence for conjugative withdrawal by π (d-p) bonding in the p-$\overset{+}{S}Me_2$ group has been reported by several authors (7).

TABLE 1

Second order rate coefficients ($l.mole^{-1}sec^{-1}$) for nitration of dimethylphenylsulphonium methyl sulphate in aqueous sulphuric acid at 25°C. (*)

H_2SO_4(%wt)	10^3 K_2	H_2SO_4(%wt)	10^3 K_2	H_2SO_4(%wt)	10^3 k_2
84.2	0.131	89.9	3.066	94.2	2.012
85.6	0.301	90.8	2.916	94.5	1.924
87.3	0.960	90.9	2.894	95.7	1.729
88.3	1.751	92.1	2.542	97.1	1.459
89.8	3.047	93.2	2.246	98.0	1.330

(*) $Ph\overset{+}{S}Me_2 = 3\cdot10^{-4}$ m/l., $HNO_3 = 2\cdot10^{-2}$ m/l.

Acknowledgement.- We thank the Consiglio Nazionale delle Ricerche (Roma) for support.

REFERENCES

1) N.C.Marziano, E.Maccarone and R.Passerini, *J.Chem.Soc.* (B) 745 (1971);
2) A.Gastaminza, T.A.Modro, J.H.Ridd and J.H.P.Utley, *J.Chem.Soc.* (B) 534 (1968); A.Gastaminza, J.H.Ridd and F.Roy, *J.Chem.Soc.* (B) 684 (1969);
3) H.M.Gilow and G.L.Walker, *J.Org.Chem.* **32**, 2850 (1967);
4) B.A.Bolto and J.Miller, *Australian J.Chem.* **9**, 74 (1956);
5) R.G.Combes, R.B.Moodie and K.Schofield, *J.Chem.Soc.* (B) 800 (1968);
6) D.P.Craig, *Pure appl.Chem.* **4**, 4 (1954); D.P.Craig and E.A.Magnusson, *J.Chem.Soc* 4895 (1956);
7) F.G.Bordewell and P.J.Boutan, *J.ChemSoc.* **78**, 87 (1956); R.W.Taft and J.W. Rakshys, *J.Am.Chem.Soc.* **87**, 4387 (1965); C.C.Price and S.Oae, "Sulphur bonding" Ronald Press Co.New York, N.Y. (1962) cap.5; J.Miller, "Aromatic Nucleophilic Substitution" Elsevier Publ.Co (1968) pag.72.