

suppressed in favour of recombination as demonstrated by the small amount of carbonyl compounds and amino-acids in the irradiated solution.

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
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<sup>4</sup> Kopoldová, J., Liebster, J., and Babicky, A., *Intern. J. App. Rad. and Isotopes* (in the press).  
<sup>5</sup> Kopoldová, J., Liebster, J., and Babicky, A., *Intern. J. App. Rad. and Isotopes* (in the press).  
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## CHEMISTRY

### Methanolysis of 2,4-Dinitrophenyl *p*-Toluene Sulphonate

THE methanolysis of 2,4-dinitrophenyl *p*-toluene sulphonate has been investigated, in continuance of a series of investigations of the methanolysis of nitrophenyl esters<sup>1,2</sup> both under initially neutral conditions and in the presence of tertiary bases, namely, pyridine and its methyl derivatives. In the cases of picryl acetate<sup>1</sup> and 2,4-dinitrophenyl acetate<sup>2</sup> both the neutral and base-catalysed reactions show acyl-oxygen fission:

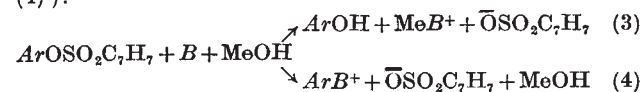


(where  $Ar = NO_2$  ). In the case of picryl benzoate<sup>1</sup> under initially neutral conditions, along with acyl-oxygen fission (1), there also occurred some aryl-oxygen fission (2):



Reaction (2) did not, however, occur in the presence of tertiary bases. The order of the catalytic constants ( $k_2^B$ ) are in each case  $k_2^{Py} > k_2^{Co} > k_2^{Lu} > k_2^{Pi}$ , whereas the basic strengths are in the order 2,4,6-collidine > 2,6-lutidine > 2-picoline > pyridine. Thus specific and general base catalysis are ruled out. The mechanism is thus nucleophilic catalysis.

The catalysis of the methanolysis of 2,4-dinitrophenyl *p*-toluene sulphonate by pyridine, 2,6-lutidine and 2,4,6-collidine has been investigated at 45° C. The reaction follows two paths leading to 2,4-dinitrophenol (reaction (3)) and the 2,4-dinitrophenyl pyridinium ions (reaction (4)):



Reactions (3) and (4) were followed chemically by measuring respectively the rate of 2,4-dinitrophenol and complex formation. This is essentially a modification of the method of Olivier and Berger<sup>3</sup>. In the case of pyridine, reaction (4) accounts for some 45 per cent of the total reaction, while for 2,4,6-collidine the amount of reaction going by this path was only 14 per cent. None of the reaction in the presence of 2,6-lutidine appeared to go by this route. The reaction products have all been isolated and identified by comparison of the analysis figures and infra-red spectra

with those of the pure compounds. The nature of the products enables the mechanism to be postulated<sup>4</sup>. In the cases of pyridine and 2,4,6-collidine it is concurrent sulphur-oxygen fission (reaction (3)) and acryl-oxygen fission leading to the complex (reaction (4)). In the case of 2,6-lutidine, only the former process is observed.

For a given concentration of base, good first order rate-coefficients were obtained for reaction (3), and these, when divided by the base concentration, yielded the catalytic constants. It is found that  $k_2^{Py} > k_2^{Co} > k_2^{Lu}$ , which is the same order as was found for the picryl compounds<sup>1</sup> and for 2,4-dinitrophenyl acetate<sup>2</sup>. Once again specific and general base catalysis can be eliminated as possible mechanisms and so nucleophilic catalysis must occur, the catalytic constants being determined in part by the basic strengths and in part by the steric effect of the methyl groups of the base. Reaction (4) is also subject to steric effects as the rate coefficients decrease in the order pyridine 2,4,6-collidine 2,6-lutidine.

Further investigations are being made into the reactions in the presence of 2- and 4-picoline, and in the light of these a fuller discussion of the mechanism will be presented elsewhere.

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<sup>3</sup> Olivier and Berger, *Rec. Trav. Chim. Pays-bas*, **40**, 609 (1927).

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### Formation of Phase Test Intermediate of Chlorophyll by Electrolytic Reduction

IN the course of electrolytic and polarographic studies on chlorophyll and related compounds, we have found that reduction of chlorophyll *a* and *b* in aprotic solvents involves an unusual sequence of events which differ markedly from those observed in protolytic solvents<sup>1,2</sup>.

d.c. Polarographic measurements were made in dimethylsulphoxide solvent (distilled from calcium hydride), using 0.1 M tetrapropylammonium perchlorate as supporting electrolyte and an aqueous calomel anode, taking precautions to minimize water diffusion. Controlled potential reductions were carried out at a platinum gauze cathode, using a mercury pool anode and reference aqueous calomel electrode. The electrolysis apparatus permitted also thorough deoxygenation and determination of the absorption spectrum of the solution.

Polarographic results for chlorophyll *a* and some derivatives (Fig. 1) are presented in Table 1. Two waves were observed for all compounds<sup>1,2</sup> and heights for both waves were linear in the square root of the mercury head. The spectral changes following electrolytic reduction of ethyl chlorophyllide *a* at the plateaux of either the first (-1.3 V) or second (-1.6 V) polarographic waves are given in Fig. 2. The resultant spectrum (3, Fig. 2) is unequivocally that of the phase test intermediate (*V*, Fig. 1), as shown by comparison with published spectra<sup>3,4</sup> and by formation of the identical spectrum on addition of aqueous potassium hydroxide. In further agreement with this identification are the following observations on the electrolysed solution: (1) no electron spin resonance was obtained; (2) addition of deoxygenated boric acid solution gave quantitative recovery of *I*; (3) bubbling with air or addition of iodine regenerated a