

Nonaqueous Titration of Some Nitro Compounds Containing the Dinitrophenyl Group

BENGT SMITH and ÅKE HAGLUND

Institutionen för Organisk kemi, Chalmers Tekniska Högskola, Göteborg, Sweden

It is demonstrated that various types of nitro compounds obtained in the characterization of such organic compounds as alcohols, phenols, mercaptans and amines can be titrated quantitatively in acetone or pyridine using tetra-*n*-butylammonium hydroxide in benzene-methanol as titrant.

In the characterization of organic compounds various types of nitro derivatives have been utilized to a great extent. The reason for this is the excellent crystallization properties shown by the derivatives formed. The identification is generally based on melting point determination which method, however, is often hampered by the fact that the melting points of two or several compounds lie close together. Although other methods are available for the identification and analysis of the nitro derivatives, *e.g.* paper chromatography, absorption spectrophotometry and quantitative reduction, it is felt that a rapid titration method for determining the equiv. weight should be a useful adjunct to the existing methods.

Among organic compounds which are often characterized in the form of nitro derivatives are alcohols, phenols, thiols, amines, aldehydes and ketones. Thus to characterize alcohols and phenols they may be transformed into 2,4-dinitrophenyl ethers or 2,4-dinitrobenzoates and thiols into 2,4-dinitrophenyl thioethers. By reaction with 2,4-dinitrochlorobenzene, 2,4-dinitrobenzoyl chloride and 2,4-dinitrobenzaldehyde, amines may be transformed into *N*-substituted 2,4-dinitroanilines, 2,4-dinitrobenzamides and Schiff's bases, respectively, all of which are useful for characterization purposes. The transformation of aldehydes and ketones into 2,4-dinitrophenyl hydrazones is, perhaps, the most wellknown example of the utilization of nitro derivatives in the characterization of organic compounds.

The latter group was recently investigated by Sensabaugh *et al.*¹ and found to be titratable using tetra-*n*-butylammonium hydroxide in pyridine. The base consumption was believed to be due to the presence of an acidic hydrogen atom at nitrogen. The bulk of the derivatives mentioned above contain no

acidic hydrogen atoms. Nevertheless there seemed to be a good chance to analyse them using a titration procedure similar to that used by Sensabaugh *et al.* Meisenheimer² in 1902 showed that certain nonacidic nitro compounds, *e.g.* nitro derivatives of aromatic hydrocarbons and ethers, reacted with bases forming crystalline adducts. Later, Brockmann and Meyer³ reported the titratability of aromatic nitro hydrocarbons and one nitro ether in nonaqueous solvents*, and recently nonaqueous titration was utilized by Fritz *et al.*⁴ for the quantitative analysis of some aromatic nitro hydrocarbons. The background of the reaction will be given below.

The application of a nonaqueous titration procedure to the analysis of the nitro derivatives mentioned previously was found to give results accurate enough for the purpose, although the precision was not as good as in the titration of certain other acidic compounds, *e.g.* phenols, *cf.* Table 1. The titration was performed in acetone or pyridine using tetra-*n*-butylammonium hydroxide as the titrant. Acetone was found to be of more general utility than pyridine,

* No values were given, however.

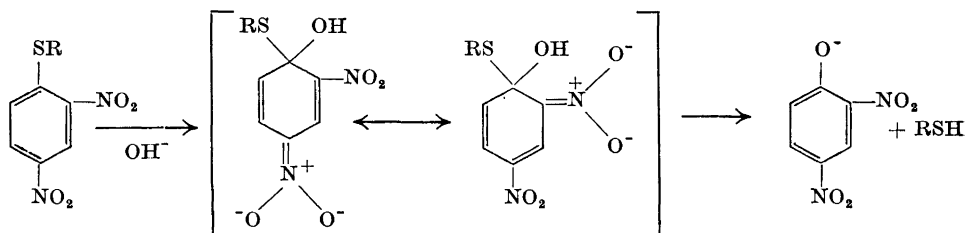
Table 1. Titration of dinitrophenyl derivatives in acetone or pyridine using tetra-*n*-butylammonium hydroxide.

Type	Compound Name	Base consumption, equiv. per mole		Derivative used for the character- ization of
		Solvent acetone	Solvent pyridine	
Ester	Methyl 3,5-dinitrobenzoate	1.03	1.02	Alcohols and Phenols
	Ethyl 3,5-dinitrobenzoate	1.02	1.04	
	<i>n</i> -Propyl 3,5-dinitrobenzoate	1.02	1.02	
	Phenyl 3,5-dinitrobenzoate*	1.00	1.01	
	Methyl 2,4,6-trinitrobenzoate	1.02	1.00	
Ether	2,4-Dinitrophenyl methyl ether	0.98	0.97	Alcohols and Phenols
	2,4-Dinitrophenyl ethyl ether	1.00	0.98	
	2,4-Dinitrophenyl phenyl ether**	1.04	0	
	2,4,6-Trinitrophenyl methyl ether	1.01	1.00	
Thioether	2,4-Dinitrophenyl <i>tert.</i> butyl thioether	1.05	1.35	Thiols
Amine	2,4-Dinitrophenyl <i>N-n</i> -propylamine	1.01	0.98	Amines
	2,4-Dinitrophenyl <i>N</i> -benzylamine	1.01	1.03	
	2,4-Dinitrophenyl <i>N,N</i> -dimethylamine	1.02	0	
Amide	<i>N-n</i> -Propyl 3,5-dinitrobenzamide	1.01	1.01	Amines
	<i>N</i> -Benzyl 3,5-dinitrobenzamide	1.03	0.99	
	<i>N,N</i> -Dimethyl 3,5-dinitrobenzamide	0.97	0.99	
Schiff's base	<i>N-n</i> -Propyl 3,5-dinitrobenzalamine	0.98	1.01	Amines
	<i>N</i> -Benzyl 3,5-dinitrobenzalamine	0.99	0.98	

* Two inflexion points were obtained.

** The base consumption of this compound was rather varying and appreciably higher values were sometimes obtained.

since certain compounds could not be titrated in the latter solvent or gave high values. The excess base consumption obtained for 2,4-dinitrophenyl *tert.* butyl thioether might be due to a partial splitting of the base adduct, *e.g.*



A similar explanation might be advanced in certain other cases, where a tendency to high values was observed, *e.g.* for 2,4-dinitrophenyl phenyl ether. For phenyl 3,5-dinitrobenzoate two inflexion points were obtained. The first one, which we believe is due to the addition of base, corresponded to a consumption of 1 equiv. of base per mole. The second inflexion point at about 1.6 equiv. of base per mole might be connected with the transesterification reaction which was recently⁵ reported to take place with phenolic esters in the presence of the tetra-*n*-butylammonium base titrant. While the reaction of the esters, ethers, Schiff's bases and of the *N,N*-disubstituted amines and benzamides must involve addition of base to the molecule, the titratability of the *N*-monosubstituted amines and benzamides is most likely due to abstraction of an acidic hydrogen atom from the nitrogen atom.

EXPERIMENTAL

Materials. Most of the nitro compounds used in this investigation were prepared in this laboratory. Their purity was ascertained by melting point determination.

Titration procedure. The titrations were performed essentially as described by Fritz and Hammond⁶ using 0.1 N tetra-*n*-butylammonium hydroxide in benzene-methanol as titrant and acetone or pyridine as solvent. The solvents were of reagent grade and the pyridine dried over potassium hydroxide and distilled before use. Glass calomel electrodes were used and the titration followed by means of a Radiometer Titrator model TTT 1.

Acknowledgement. The authors wish to thank the *Town Council of Gothenburg* for financial support of this work.

REFERENCES

1. Sensabaugh, A. J., Cundiff, R. H. and Markunas, P. C. *Anal. Chem.* **30** (1958) 1445.
2. Meisenheimer, J. *Ann.* **323** (1902) 205.
3. Brockmann, H. and Meyer, E. *Naturwiss.* **40** (1953) 242.
4. Fritz, J. S., Moye, A. J. and Johnson Richard, M. *Anal. Chem.* **29** (1957) 1685.
5. Smith, B. and Haglund, Å. *Acta Chem. Scand.* **14** (1960) 1349.
6. Fritz, J. S. and Hammond, G. S. *Quantitative Organic Analysis*, J. Wiley and Sons, Inc., New York 1957, p. 266.

Received November 30, 1960.