Expt.	"A" Cc.	Glucose Cc.	Ratio
1	10.02	8.56	1.171
2	11.11	9.54	1.165
3	10.01	8.56	1.169
		Av.	1.168
	Maximum variation from av.		0.26%

Using the dextrose value of the Fehling solution as above determined, the percentage of reducing sugar in the sample may be readily calculated, giving for Expt. 3 above, 67.09% of dextrose.

Since this method depends upon the complete precipitation of the copper as cuprous oxide, it seemed advisable to check these results gravimetrically. This was done by filtering on a Gooch crucible the precipitate from Expt. 3, drying and weighing it. The weight of the cuprous oxide thus found was 0.1969 g. Since the amount of cuprous oxide theoretically obtainable from 10.01 cc. of Fehling solution containing 0.01745 g. of copper per cc. is 0.1966 g., the difference between the two weights, 0.3 mg., shows that the end-point had been determined in a satisfactory manner.

Summary

A rapid method has been described for the volumetric determination of reducing sugars by means of Fehling solution, using the electrometric method for ascertaining the end-point. The uncertain personal element in determining the end-point is thus eliminated.

The method, as checked gravimetrically, is found to be accurate.

No work has yet been done on the determination of very small amounts of reducing sugars, or upon the effect of the presence of large quantities of other sugars such as sucrose.

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THE REACTION OF NITROSYL CHLORIDE ON TOLUENE

By E. V. Lynn and Helen L. Arkley

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Some time ago one of us found[1] that nitrosyl chloride will readily react with normal heptane in the sunlight to produce a blue material which easily changes to a colorless oil. The blue compound was later shown[2] to be nitroso-dipropylmethane and the rearranged oil, dipropyl-ketone oxime. It was also demonstrated that this reaction is probably general for all of the paraffin hydrocarbons, a conclusion reached mainly because

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[1] Lynn, This Journal, **41,** 368 (1919).

[2] Lynn and Hilton, *ibid.*, **44,** 646 (1922).

gasoline and petroleum ether give a similar blue color with nitrosyl chloride.

In experimenting with various substances, it was found that benzene could not be induced to react at all with the reagent, even in sunlight; a sample of benzene solution was kept for months without any change in the brown color of the nitrosyl chloride. In view of this fact, paraffin derivatives of benzene should react in such a way that only the alkyl radical is attacked. Toluene, the simplest alkyl drivative, should give, according to previous experience, phenylnitrosomethane rearranging to benzaldoxime. $C_6H_5—CH_3 + NOCl \longrightarrow C_6H_5—CH_2—NO + HCl$. $C_6H_5—CH_2—NO \longrightarrow C_6H_5—CH = N—OH$. Experiment has fully demonstrated the correctness of this reasoning, as toluene reacts readily in the sunlight with nitrosyl chloride producing benzaldoxime, which has been converted to benzaldehyde, benzoic acid and benzanilide in the usual way.

Experimental Part

The nitrosyl chloride was prepared as previously described[2] by the reaction of nitrosyl sulfate and sodium chloride. The toluene was first dried over sodium hydroxide and then distilled, the portion boiling between 110° and 112° being used. This was saturated with the gas, giving a dark red-brown liquid. In the dark at room temperature there was practically no change in the appearance, but after some time a heavy, insoluble oil and some gas were formed. In the sunlight the reaction was quite rapid, producing large quantities of gas, mostly hydrogen chloride, and an amount of the heavy oil equal to about 3% of the toluene used. In later experiments the saturated solution was exposed to the sunlight at temperatures below 10°. In these cases the reaction proceeded somewhat more slowly and, in place of the oil, there were deposited beautiful, white, iridescent, feathery crystals. In all experiments the color of the solution disappeared with the formation of the precipitate. There was, however, no intermediate production of a blue color and one can only conclude that phenylnitrosomethane is very unstable.

In subsequent changes the oil and crystals acted alike and, since it was just as easy to produce the latter and more convenient to work with them, they were employed in the reactions recorded below. The crystals had an indefinite melting point, from 35° to 70°. They were dissolved in sodium carbonate solution and extracted with ether, evaporation of the latter leaving characteristic crystals of β-benzaldoxime, melting at 128°. The primary product was, therefore, undoubtedly a mixture of the hydrochlorides of both benzaldoximes, since the above procedure transforms the α to the β form. Hydrolysis of the oxime with dil. acid gave an oil identified by its odor as benzaldehyde. It was oxidized by nitric acid and the resulting benzoic acid was precipitated on cooling, and melted at 118°. It was further identified by converting to its ferric salt and to benzanilide, m. p. 158°.

The amount of benzaldoxime crystals obtained is practically that calculated based upon the nitrosyl chloride used, about 3% by weight of the toluene. The time required is dependent upon the temperature and upon the intensity of the sunlight but in no case was it longer than 2 hours. Under the right conditions the reaction could undoubtedly be made to proceed more rapidly and probably continuously. Whether the process can be utilized commercially under the influence of some catalyst is a problem which is at present engaging our attention. Furthermore, we are studying the action of nitrosyl chloride on other substances and will report the results later.

Summary

Nitrosyl chloride readily reacts with toluene in the sunlight to produce crystals of benzaldoxime hydrochloride, from which benzaldoxime, benzaldehyde, benzoic acid and benzanilide can be prepared in the usual way.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

AN ELECTROCHEMICAL METHOD OF STUDYING IRREVERSIBLE ORGANIC REDUCTIONS

Preliminary Paper

BY JAMES B. CONANT AND ROBERT E. LUTZ

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The reversible reduction of such organic substances as anthraquinone and benzoquinone can be studied easily by electrochemical methods and the experimental results can be quantitatively expressed in the terms of a general thermodynamic equation.[1] This has not been true, hitherto, of the *irreversible* reduction processes which are so common in organic chemistry. In a recent paper[2] it was pointed out that the irreversible reductions brought about by catalytic hydrogenation cannot be interpreted even qualitatively by means of an electrochemical explanation; on the other hand, the irreversible reductions which are caused by such reducing agents as titanous chloride and chromous chloride are in qualitative agreement with a definite scheme of oxidation-reduction potentials. We have con-

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[1] (a) Haber and Russ, *Z. physik. Chem.*, **47**, 257 (1904). (b) Granger and Nelson, THIS JOURNAL, **43**, 1401 (1921). (c) W. M. Clark, *J. Wash. Acad. Sci.*, **10**, 255 (1920). (d) Biilmann and Lund, *Ann. chim.*, **16**, 321 (1921). (e) Conant, Kahn, Fieser and Kurtz, THIS JOURNAL, **44**, 1382 (1922). (f) LaMer and Baker, *ibid.*, **44**, 1954 (1922). (g) Conant and Fieser, *ibid.*, **44**, 2480 (1922).

[2] Conant and Cutter, THIS JOURNAL, **44**, 2651 (1922).