

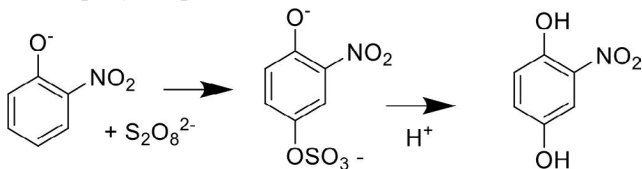
INTRODUCTION TO A TRANSLATION OF “UEBER NITROHYDROCHINON” BY KARL ELBS

E. J. Behrman, Department of Chemistry & Biochemistry, The Ohio State University, Columbus, OH, Behrman.1@osu.edu.

D. M. Behrman, Department of Mathematics & Chemistry, Somerset Community College, Somerset, KY

Manuela Davis, Somerset Community College, Somerset, KY

Karl Elbs (1858-1933) was a distinguished chemist at the University of Freiburg (1) specializing in electrochemistry. He was the author of one of the first compendia summarizing methods for the preparation of organic compounds, a very popular book on storage batteries (five editions), and a textbook on laboratory methods for electrolytic preparations which was published in two German editions and also in French and English translations. For details, see ref. 1. He also has two organic reactions named after him, the Elbs Reaction, a method for the synthesis of anthracenes (2) and the Elbs Oxidation, a way of converting phenols to the phenol *p*-sulfate by reaction with peroxydisulfate and so to the *p*-hydroquinone, as in the scheme below.



The translation presented here is Elbs' discovery of the second reaction early in his career at Freiburg. It has been the subject of many reviews (3-5) with hundreds of citations. It is instructive for today's chemists to understand how structural assignments were made in the days before the existence of our current spectroscopic tools. Purity was established by elemental analysis (still a requirement by the better journals) and structure by the method of formation, relationship to known compounds, the formation of predicted derivatives, and cryoscopic determination of the molecular weight. Elbs used the

molar freezing point depression of naphthalene. I note that molecular weight determination using a colligative property has certain advantages. Sharp melting points were treasured. In 1893, mononitrohydroquinone was unknown although its monomethyl ether was known. Some dinitrohydroquinones, on the other hand, had been made. Salts of peroxydisulfate had been recently described by Marshall (6). Many ways of oxidizing phenol were known in 1893 (7), but, no doubt, Elbs wanted to try the effect of this new oxidizing agent and his choice of the *o*-nitrophenol was fortunate as the yields from this phenol are larger than from many others (5). It is interesting that his paper does not show that the product of reaction of *o*-nitrophenol in alkaline solution was actually the *o*-nitrophenol-*p*-sulfate, the diphenol being obtained by subsequent hydrolysis in acid, although acidification was part of his protocol. For references on this discovery see Sethna (3). It is also interesting that although Elbs properly conducted his reaction in alkaline solution as it is the phenolate ion that is the reactive species, he later states, incorrectly, that the reaction proceeds at all pH values. Richter (8) confirmed the identity of Elbs' product by an alternative synthesis via nitration of hydroquinone monobenzoate followed by alkaline hydrolysis. The portions of the translation in brackets [] are interpolations by the translators.

We thank the referee for many excellent emendations.

References and Notes

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About the Authors

E. J. Behrman is Professor Emeritus of Chemistry & Biochemistry at the Ohio State University

D. M. Behrman is Professor of Mathematics & Chemistry (retired) at Somerset Community College

Manuela Davis is Staff Instructor at Somerset Community College

PRIMARY DOCUMENTS ON NITROHYDROQUINONE

Karl Elbs

"Ueber Nitrohydrochinon," *J. prakt. Chem.* [n.F.], **1893**, *48*, 179-185

Translated by E. J. Behrman, D. M. Behrman, Manuela Davis

Until now, mononitrohydroquinone has only been known in the form of several of its derivatives. Now it is shown that nitrohydroquinone can be made by direct oxidation of *o*-nitrophenol with ammonium peroxydisulfate (1).

A solution of 35 g [0.25 mol] of *o*-nitrophenol, 50 g [1.25 mol] of sodium hydroxide, and 50 g [0.22 mol] of ammonium peroxydisulfate in 1500 g of water was allowed to stand for 1.5-2 days with occasional shaking. Then the mixture was acidified with sulfuric acid, the unchanged nitrophenol separated by steam distillation, a small amount of resinous material removed by filtration, and then extracted with ether. The ether extract, after evaporation, gave crystals of nitrohydroquinone which after one recrystallization from water or dilute ethanol

is pure. The yield is between 30-40% based on the starting material. Also, about half of the initial nitrophenol was recovered unchanged but increasing the amount of ammonium peroxydisulfate does not increase the yield of nitrohydroquinone but rather diminishes it.

Mononitrohydroquinone crystallizes as rhombohedra or as pyramids which frequently grow together like a cockscomb. The color varies from yellow-red to garnet-red. It melts without decomposition between 133-134° and then solidifies within a few degrees of cooling in crystalline form. There is but slight tendency for sublimation in spite of marked volatility already at 100°. It is not subject to steam distillation. It is very soluble in ether and alcohol, less in acetic acid and hot water, moderately in cold water, hardly at all in benzene, and even less soluble in petroleum ether. It is best crystallized from water or