Negative Chemical Ionization as a Model for Reactions in Solution: New Nucleophilic Reactions of Superoxide

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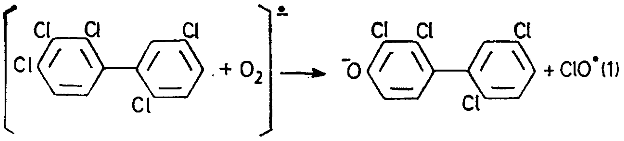
Summary Anionic gas phase reactions between oxygen and *p*-chloronitrobenzene or iodobenzene have proved to be useful guides to the corresponding reactions in solution which result in the formation of phenols.

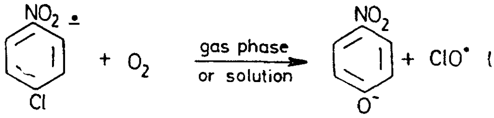
THIS report discusses the first examples of reactions in solution that have been discovered on the basis of examination of ion–molecule reactions in a chemical ionization mass spectrometer. Correlations[1] and discrepancies[2] between ion–molecule reactions under chemical ionization[3] (CI) and ion cyclotron resonance conditions and in solution are well known. In view of the relative ease of obtaining CI and negative chemical ionization[4] (NCI) data it seems reasonable to take advantage of the reactivity correlations to guide the study and development of new ion–molecule reactions in solution. The following discussion focuses on new anionic reactions involving oxygen (O_2) as one reactant; however, many other systems should be susceptible to this type of development.

In studies of the NCI mass spectra of polychlorobiphenyls (PCB's) we consistently noted prominent $(M - 19)^-$ ions in the spectra of PCB's with four or more chlorines. When the PCB NCI spectra were obtained with rigorous exclusion of oxygen gas the $(M - 19)^-$ ions were absent from the spectrum. These results can be rationalized for 2,3,4,2',5'-pentachlorobiphenyl as shown in equation (1).



The location of the charges in equation (1) is uncertain. The relatively low abundance of the superoxide anion (*m/e* 32) in our spectra (generally $< 1\%$), makes us favour reaction from the molecule anion. The low abundance of hypochlorite anions (*m/e* 51) likewise suggests that this fragment is formed as a radical. The same reaction has been observed with an atmospheric pressure ionization source[5] in which the reactant was the superoxide anion. It is reasonable to expect that the transition states for reaction will be the same for either $M^- + O_2$ or $M + O_2^-$. In either case it is likely that the reaction occurs from the organic radical anion and oxygen.[6]

With isobutane as the reagent gas (1 Torr) and with rigorous exclusion of oxygen the NCI spectra of *p*-bromobenzophenone, 2,4-dinitrochlorobenzene, and 4-nitrochlorobenzene were all dominated by the respective molecule anions (*m/e* 260, 202, and 157, respectively). Upon addition of 0·2 Torr of oxygen gas to the reagent gas mixture the molecule anions were replaced as the base peak by the corresponding $(M - X + O)$ anions [equation (2)].



This oxygen exchange reaction has been reproduced in solution for 4-nitrochlorobenzene by the two following methods, the first involving the organic anion, and the second the superoxide anion which probably transfers an electron to the chloronitrobenzene prior to reaction.[6]

A solution containing sodium (2 equiv.) in liquid ammonia under dry nitrogen was added to 4-nitrochlorobenzene dissolved in tetrahydrofuran. Formation of the radical anion was immediate as judged by the colour of the solution, and dry oxygen gas was bubbled into the mixture. After 20 min the reaction was quenched with anhydrous methanol,

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neutralized with HCl, and worked up. The products included *p*-nitrophenol (33% based on recovered starting material), a trace of 4,4′-dinitrobiphenyl and the expected aminolysis products.[7] If oxygen was excluded in the procedure the yield of *p*-nitrophenol was $< 0\cdot1\%$. The same conversion was accomplished by adding 4-nitrochlorobenzene to a solution that contained potassium superoxide (2 equiv.) dissolved in dry hexamethylphosphoramide containing 18-crown-6 ether[8] (2 equiv.) under dry oxygen. After 4 h at room temperature the mixture was quenched with anhydrous methanol and acidified immediately with conc. HCl. Upon acidification chlorine gas was evolved, indicating that the hypochlorite radical which is produced in the reaction is further reduced by superoxide to the hypochlorite anion. *p*-Nitrophenol was the only major product (76% based on recovered starting material).

In a related experiment we examined the NCI mass spectrum of iodobenzene in the presence of 0·7 Torr of oxygen and 0·1 Torr isobutane (source temperature 319 K). The only significant high mass ion in this spectrum other than the iodide base peak (*m/e* 127) corresponded to $(M - H + O)^-$, *i.e.* *m/e* 219 (0·4%). The iodobenzene molecule anion in THF—NH_3 was treated with oxygen under conditions identical to those of the first 4-nitrochlorobenzene experiment described above. In addition to the expected diphenylamine and biphenyl, we isolated *p*-iodophenol (4%), spectroscopically and chromatographically identical to a purified authentic sample; phenol was not detected in the product mixture. The displacement of hydrogen rather than halogen and the exclusive production of the *para* isomer are intriguing. The directive influence is probably similar to those found in the Birch reduction.

Nucleophilic reactions of superoxide with aliphatic halides are known;[9] however, in the reported cases the products were identified as organic hydroperoxides.

NCI mass spectra may be obtained and generally interpreted for a given system within a matter of minutes. For this reason we expect that NCI spectra will be increasingly used as a guide to potential new reactions in solution.

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[1] F. H. Field, *J. Amer. Chem. Soc.*, **1969**, **91**, 2827.
[2] J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, 1970, **92**, 6986.
[3] F. H. Field, *Accounts Chem. Res.*, 1968, **1**, 42.
[4] H. P. Tannenbaum, J. D. Roberts, and R. C. Dougherty, *Analyt. Chem.*, 1975, **47**, 49.
[5] I. Dzidic, D. I. Carrol, R. N. Stillwell, and E. C. Horning, *J. Amer. Chem. Soc.*, 1974, **96**, 5258; I. Dzidic, personal communication.
[6] R. Paupko and I. Rosenthal, *J. Phys. Chem.*, 1973, **77**, 1722.
[7] G. F. White and C. A. Kraus, *J. Amer. Chem. Soc.*, 1923, **45**, 768.
[8] J. S. Valentine and A. B. Curtis, *J. Amer. Chem. Soc.*, 1975, **97**, 224.
[9] M. V. Merritt and D. T. Sawyer, *J. Org. Chem.*, 1970, **35**, 2157.