

The corresponding values for anthracene are in much better accord. (The anthracene D_{el} value of 6.6×10^{-5} cm.²/sec. in MeCN is based on anodic oxidation and clearly is a case of incorrect assignment of n_T .) Small differences between D_{tr} and D_{el} as shown in Table I for naphthalene in D-W, and biphenyl and anthracene in DMF, may well be explained by overlap of the inherent inaccuracies of the two methods. We believe the probable error in the D_{tr} values is *ca.* $\pm 5\%$ and about $\pm 2\%$ in the viscosities. The probable errors in $(D\eta)_{tr}$ are then about $\pm 7\%$ although the data given appear to be fortuitously less than these limits. The unmodified Ilkovic equation was used in all polarographic calculations. Further, very rapid drop times are encountered at the high negative reduction potentials of these compounds. Diffusion current measurements under these conditions are subject to considerable error. In addition there may be smaller error contributions from differences in supporting electrolytes and purity of the solvents used in the various polarographic studies.

It is difficult to access the errors in the D_{el} value of 0.78×10^{-5} cm.²/sec. for anthracene obtained by alternating current polarography.⁷ Although Aten indicates an uncertainty of $\pm 2\%$ in this D value, the value of 1.32×10^{-5} cm.²/sec. determined by d.c. polarography⁹ is in agreement with D_{tr} in the sense discussed above.

The importance of the present work lies not only in establishing what appears to be a reliable set of D_{tr} values for several hydrocarbons (from which approximate D values in other solvents can be obtained *via* the $D\eta$ relationship) but also in its implications in the study of electrode processes. Especially for organic substances reduced or oxidized near background potentials, this study emphasizes that limiting currents may give false impressions of n_T . Electrode mechanisms originating with n_T calculations should be strongly supported by independent information.

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Paramagnetic Intermediates in the Condensation of Nitrosobenzene and Phenylhydroxylamine¹

Sir:

Reaction of nitrosobenzene (0.005 *M*) and phenylhydroxylamine (0.005 *M*) in the presence of 0.05 *M* potassium *t*-butoxide in deoxygenated dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) solution at $23 \pm 1^\circ$ produces essentially a quantitative yield of nitroso-

(1) Reactions of Resonance Stabilized Anions. XVI. Work supported by grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of these funds.

benzene radical anions² in <0.5 sec. In this solvent

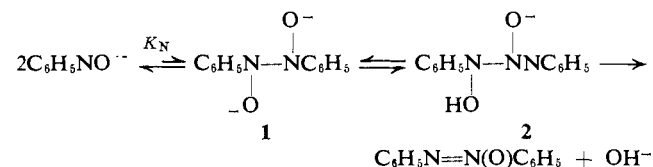


the radical anion decays slowly over a period of days.

In the absence of added base in dimethyl sulfoxide, *t*-butyl alcohol, ethanol, or benzene the reaction of nitrosobenzene (0.005 *M*) and phenylhydroxylamine (0.005 *M*) gives rise to low concentrations ($\sim 10^{-4}$ *M*) of phenyl nitroxide ($C_6H_5NHO\cdot$),³ detected and identified by the e.s.r. spectrum shown in Figure 1, that persist for a period of hours, even in the presence of oxygen. Presumably the phenyl nitroxide is slowly formed and slowly destroyed. After the e.s.r. signal has decayed an essentially quantitative yield of azoxybenzene can be isolated.

In ethanol containing sodium hydroxide, nitrosobenzene and phenylhydroxylamine rapidly react to yield up to 96% of azoxybenzene. Nitrosobenzene radical anions can be detected and identified under flow conditions² but rapidly decay when the flow is stopped. Figure 2 illustrates a stopped flow experiment of a solution 0.005 *M* in nitrosobenzene, 0.005 *M* in phenylhydroxylamine, and 0.05 *M* in sodium hydroxide after mixing.⁴ The maximum concentration of nitrosobenzene radical anion detected (~ 0.005 *M*) occurred at the fastest flow rate, which represented a flow time of 0.5 sec. between mixing and detection. Under flow conditions the mixed solution underwent a blue to green to yellow color transformation in a matter of seconds.

The decay curve for nitrosobenzene radical anions given in Figure 2 follows second-order kinetics from a nitrosobenzene radical anion concentration of 0.005 to 0.0001 *M* with an empirical rate constant of 1.40×10^2 l./mole-sec. The kinetic and e.s.r. results suggest the following rapid equilibrium in the condensation reaction occurring in basic solution.⁵



(2) The e.s.r. spectrum is similar to that reported previously [F. J. Smentowski, *J. Am. Chem. Soc.*, **85**, 3036 (1963)]. The nitrosobenzene radical anion has restricted rotation around the bond between the aromatic ring and the nitrogen atom leading to magnetically nonequivalent *o*-hydrogen atoms. The situation is complicated by the fortuitous magnetic equivalence of one *o*-hydrogen atom and the *p*-hydrogen atom. The same behavior has been noted in the azobenzene radical anion (results of Dr. R. Konaka). For nitrosobenzene radical anion the h.f.s.c. are $a^N = 10.10$, $a_{o_1}^H = 4.02$, $a_p^H = 4.02$, $a_{o_2}^H = 3.65$, and $a_m^H = 1.29$ (ethanol, 23°).

(3) A. L. Buchachenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1120 (1963); C. J. W. Gutch and W. A. Waters, *Proc. Chem. Soc.*, 230 (1964).

(4) Nitrosobenzene in basic ethanol solutions produces a significant but low steady-state concentration of nitrosobenzene radical anion² that persists for minutes. In the presence of oxygen these solutions yield nitrobenzene while in the absence of oxygen azoxybenzene is produced [e.g., E. Bamberger, *Ber.*, **35**, 732 (1902)]. That the rapid formation of azoxybenzene described herein is not connected with this latter process is illustrated by the observation that, under the reaction conditions, nitrosobenzene and aniline condense to form azobenzene contaminated by no more than a trace of azoxybenzene [results of Dr. F. J. Smentowski]. Phenylhydroxylamine in basic solution does not give an e.s.r. signal in the absence of oxygen. In the presence of traces of oxygen the nitrosobenzene radical anion can be detected. Oxidation on a synthetic scale yields a mixture of nitrobenzene and azoxybenzene.

(5) In ether or tetrahydrofuran solution, *p*-nitrosotoluene or *p*-nitrosodiethylmethylaniline react with sodium to produce $p\text{-RC}_6\text{H}_4\text{NO}^- \text{Na}^+$,

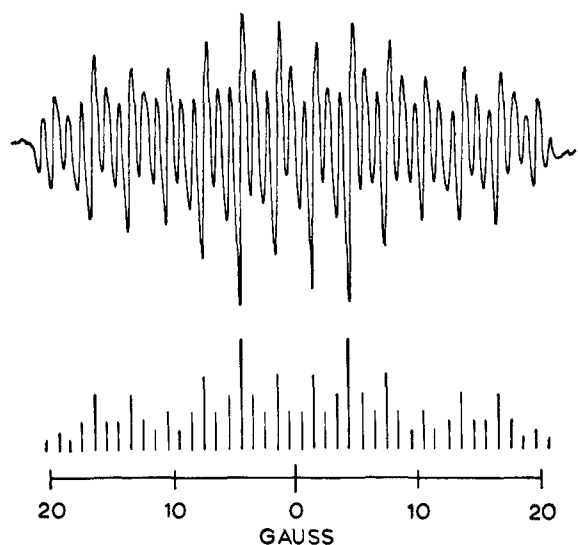


Figure 1. First derivative e.s.r. spectrum of phenylnitroxide in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%). The synthetic absorption spectrum is based on the following h.f.s.c.: $a^N = 9.10$, $a_{o.o.p}^H = 3.0$, $a_{NH}^H = 11.90$, and $a_m^H = 1.14$ gauss.

In ethanol or *t*-butyl alcohol **1** apparently undergoes protonation followed by the irreversible loss of hydroxide ion from **2** to yield azoxybenzene.⁶ Apparently in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) containing potassium *t*-butoxide the low reactivity of protons and a value of K_N that greatly favors $C_6H_5NO^-$ prevents the last step of the condensation from occurring. Although we have found no evidence for the reversal of the condensation reaction in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) at 23°, a solution of azoxybenzene (0.05 *M*) in pure dimethyl sulfoxide 50% saturated with potassium hydroxide slowly forms the nitrosobenzene radical anion, evidently *via*



Exposure of such a solution to oxygen after a 3-hr. reaction period (1×10^{-3} *M* nitrosobenzene radical anion) destroyed the e.s.r. signal. After exposure to oxygen a new e.s.r. signal slowly developed which was recognized as that of nitrosobenzene radical anion.

The present results explain why mixed condensations between XC_6H_4NO and YC_6H_4NHOH yield all possible azoxybenzenes, $XC_6H_4N(O)=NC_6H_4X$, $XC_6H_4N(O)=$

p - $RC_6H_4NO^{-2} 2Na^+$, and p - $RC_6H_4N[O^{-}Na^+]-N[O^{-}Na^+]C_6H_4R$ - p [T. Kauffmann and S. M. Hage, *Angew Chem. Intern. Ed. Engl.*, **2**, 156 (1963)]. Acidification yields the azoxybenzene derivative.

(6) Another possible interpretation is that the nitrosobenzene radical anion is first protonated, *e.g.*

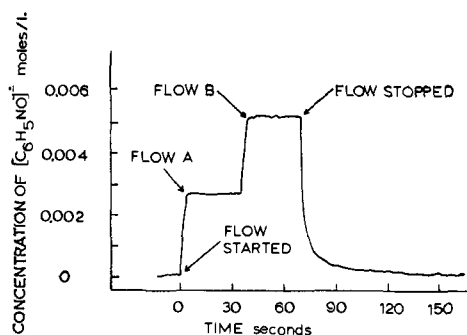
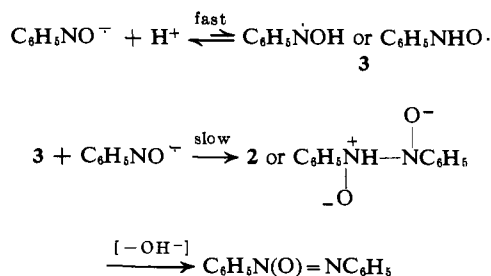
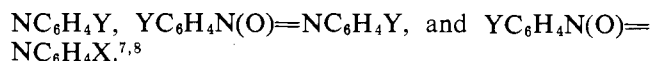


Figure 2. Concentration of nitrosobenzene radical anion measured in ethanol at $23 \pm 1^\circ$ from the reaction of a solution initially 0.010 *M* in nitrosobenzene with a solution 0.010 *M* in phenylhydroxylamine and 0.10 *M* in sodium hydroxide; flow A, radical anion detected 3 sec. after mixing; flow B, radical anion detected 0.5 sec. after mixing.



(7) E. Bamberger and E. Renaud, *Ber.*, **30**, 2278 (1897); V. O. Lukashevich, *Compt. rend. Acad. Sci., USSR*, **21**, 376 (1938); Y. Ogata, M. Tsuchida, and Y. Takagi, *J. Am. Chem. Soc.*, **79**, 3397 (1957).

(8) Various experiments with ¹⁵N- and ¹⁸O-labeled nitrosobenzene or phenylhydroxylamine [M. M. Shemyakin, V. I. Maimind, and B. K. Vaichunaite, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1260 (1957); S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc. Japan*, **36**, 728 (1963)] are consistent with the proposed condensation mechanism.

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Inhibition of an Ester Hydrolysis by Imidazole

Sir:

Since the reports of Bender and Turnquest^{1a} and Bruce and Schmir^{1b} on the imidazole-catalyzed hydrolysis of *p*-nitrophenyl acetate, many studies have been made of the catalytic properties of imidazole.^{1b-3} It is generally recognized that imidazole can enhance markedly the rate of hydrolysis (*via* a nucleophilic catalysis) of phenyl esters and thioesters, and that it may have a moderate general base catalytic effect on the hydrolysis of aliphatic esters. In this paper we report an instance of ester hydrolysis significantly inhibited by imidazole.

Aqueous solutions containing known concentrations of imidazole and sodium hydroxide were equilibrated at 25.0°. A suitable aliquot of a stock solution of methyl *trans*-cinnamate in acetonitrile was added, and the absorbance of the solution was monitored at 295 μ . From plots of $\log(A_t - A_\infty)$ vs. time the apparent first-order rate constants were evaluated. A progressive decrease in this rate constant was observed with increase in imidazole concentration. Some typical data follow (at 25.0°, in 0.0181 *N* NaOH containing 0.4% acetonitrile, with ionic strength 1.0): at molar imidazole concentrations of 0.00, 0.08, 0.16, 0.32, and 0.40, the observed first-order constants

(1) (a) M. L. Bender and B. W. Turnquest, *J. Am. Chem. Soc.*, **79**, 1652 (1957); (b) T. C. Bruce and G. L. Schmir, *ibid.*, **79**, 1663 (1957).

(2) M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1656 (1957); M. L. Bender, *Chem. Rev.*, **60**, 53 (1960); W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 675 (1960); W. P. Jencks and J. Carriuolo, *ibid.*, **83**, 1743 (1961); T. C. Bruce and S. J. Benkovic, *ibid.*, **86**, 418 (1964).

(3) J. F. Kirsch and W. P. Jencks, *ibid.*, **86**, 837 (1964).