

p-Nitrosodimethylaniline as an OH Radical Scavenger in Radiation Chemistry¹

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A method for the determination of relative rate constants for reactions with OH radicals based on the radiolysis of air-saturated solutions of *p*-nitrosodimethylaniline (RNO) is described. When 4 or 5×10^{-5} *M* solutions of RNO at pH 9 are irradiated with Co-60 γ -rays in the presence of OH scavengers, the bleaching of the RNO chromophoric group is reduced. The experimental evidence reported demonstrates that at pH 9 the method is specific for OH radicals. Simple competition kinetics are obtained in competition studies for OH radicals with Br^- , I^- , NO_2^- , N_3^- , CH_3COO^- , CH_3OH , C_2H_5OH , and other ions and compounds, and their relative rate constants are reported. The results compare favorably with other recent published values based on competition kinetics as well as measurements of absolute rate constants by the electron-pulse technique.

In an attempt to measure the formation of a postulated² ferrous pentacyanoaquo complex $[Fe(CN)_5 \cdot H_2O]^{-3}$ in the radiolysis of aqueous ferrocyanide solutions, *p*-nitrosodimethylaniline (RNO) was added to the system. A very low yield³ of green $[Fe(CN)_5 \cdot RNO]^{-3}$ was observed. In order to better understand these experiments, the radiolysis of pure RNO solutions was examined. It was found that in the radiolysis of the air-saturated aqueous solutions of RNO the bleaching of the (yellow) chromophoric group occurs, apparently only as the result of attack by OH radicals. On the basis of this system, a method has been developed for the determination of relative rate constants for OH radical reactions.

Experimental

RNO was prepared by nitrosation of dimethylaniline⁴ (monomethyl free) and was purified by two recrystallizations. For all solutions triply distilled water was used. Millimolar stock solutions of RNO were stable for periods up to several weeks when protected from strong light. These solutions were diluted to RNO concentrations as low as 4×10^{-5} *M* and were irradiated in a 1000-c. cobalt-60 γ -source. The dose rate during the course of these studies was between 7.4 and 8.5×10^{16} e.v. ml.⁻¹ min.⁻¹, as determined by the Fricke dosimeter. All experiments were done at room temperature (22–25°). Owing to the large extinction coefficient of RNO at its maximum (34,200 at 440 m μ in

neutral and alkaline solutions) it was possible to measure accurately very small changes in concentration. All measurements of optical density were performed on a Zeiss PMQ II spectrophotometer using cells with 10-mm. light path. The difference in optical density at 440 m μ between blanks and 3-min. irradiated samples of air-saturated RNO was 0.150 or higher. The system was studied mainly at pH 9, achieved by the addition of small amounts of $Na_2B_4O_7$ solution. In experiments at lower pH, H_2SO_4 and $HClO_4$ were used. The p*K* for the acid–base equilibrium between the protonated and free RNO is 3.7 and the spectral absorption maximum shifts from 440 m μ at higher pH values to 350 m μ at lower pH values. $G(-RNO)$ is constant between pH 5 and 10 and is equal to 1.1.

Results and Discussion

Figure 1 shows the absorption spectrum of unirradiated aqueous RNO solution (4×10^{-5} *M*) at pH 9 as well as that of irradiated samples. Extended irradiation will bleach out completely the 440-m μ absorption band. With longer irradiation times it may be seen that the absorption maximum shifts away from 440 m μ toward shorter wave length. This is caused by the absorption of several of the irradiation products which have absorption maxima at 428 m μ and lower. Hence the direct proportionality of the change in optical density vs. irradiation time is valid only up to 3 min. of irradiation time in the Co-60 source used. By using thin layer chromatography the separation of the irradiation products has been achieved. The major primary products appear to be nitro derivatives of the general type $R(OH)NO_2$ as well as one product with an intact NO group, possibly having an OH group in a *meta* position to it.

Competition Studies. In order to study what reactions RNO undergoes with reactive intermediates from irradiated water, scavengers of the hydrated electron⁵ and OH radical were added to RNO solutions and the effect of different concentrations of these scavengers on $G(-RNO)$ was studied. For example, a 4×10^{-5} *M* RNO solution was made 10^{-2} *M* in NO_3^- which has been reported to be a very efficient hydrated electron scavenger.⁵ Figure 2 shows the results of this study.

In this figure is plotted the change of optical density vs. irradiation time of a pure RNO system and an RNO solution containing 10^{-2} *M* NO_3^- . At low doses it is seen that the optical density difference approaches the same value asymptotically indicating that the difference arises as a result of a secondary rather than primary reaction. Thus the inference is that while the added NO_3^- did compete with dissolved O_2 for hydrated electrons, the initial $G(-RNO)$ was not affected by the

(1) (a) Parts of this paper were presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964. (b) This work was supported by the United States Atomic Energy Commission.

(2) X. Tarrago, E. Masri, and M. Lefort, *Compt. rend.*, **244**, 343 (1957).

(3) (a) I. Kraljić, unpublished results; (b) see also, I. Kraljić, M. Kopriva, and M. Pungošek, *Bull. Sci. Conseil acad. RPF Yougoslavie*, **3**, 104 (1957).

(4) A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., London, 1956, p. 573.

(5) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discussions Faraday Soc.*, **36**, 193 (1963).

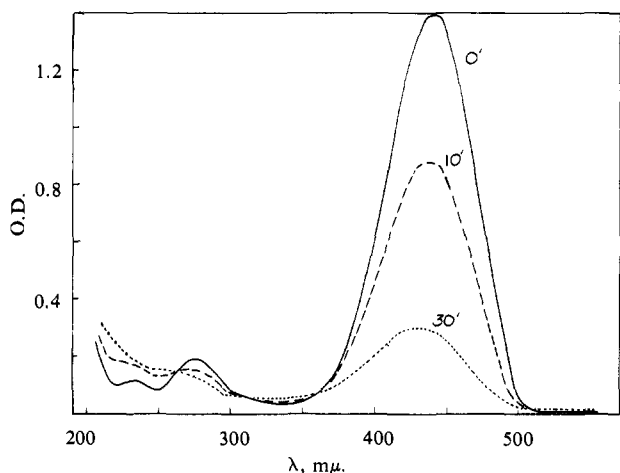


Figure 1. Absorption spectra of $4 \times 10^{-5} M$ RNO solutions at pH 9: unirradiated solution (—); 10-min. irradiated sample (---); 30-min. irradiated sample (.....); dose rate, 8.5×10^{16} e.v. ml.⁻¹ min.⁻¹.

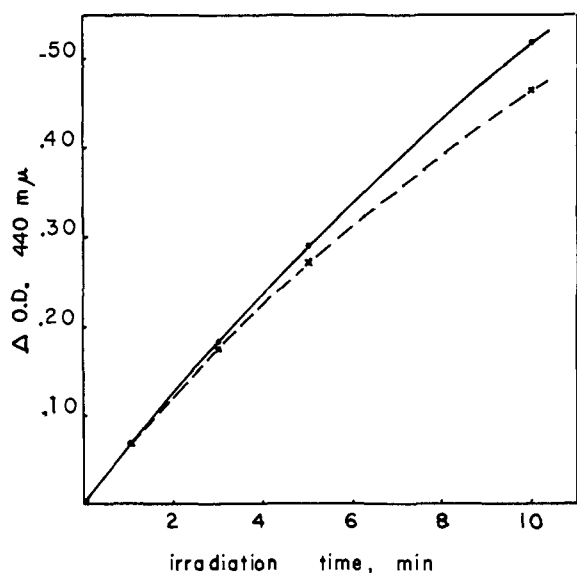


Figure 2. Effect of NO_3^- on optical density change of irradiated RNO solution at pH 9: RNO = $4 \times 10^{-5} M$ (—); RNO = $4 \times 10^{-5} M + \text{NO}_3 10^{-2} M$ (---).

presence of added NO_3^- . Instead $G(-\text{RNO})$ was strongly affected by the product of the $\text{NO}_3^- + e^-$ (aq) reaction. It has been reported by Mahlman and Schweitzer^{6a} and more recently by Allan^{6b} that NO_2^- is a major product in the radiolysis of NO_3^- . Furthermore, Schwarz⁷ reports that NO_2^- is an efficient OH scavenger. It is therefore apparent that the radiation product NO_2^- is competing secondarily with RNO for OH radicals.

Small concentrations of acetone, reported as having a bimolecular rate constant of $5.9 \times 10^9 M^{-1} \text{sec}^{-1}$ for reaction with the hydrated electron,⁵ did not affect $G(-\text{RNO})$. However, at higher acetone concentrations (above $10^{-4} M$) $G(-\text{RNO})$ decreased with increasing acetone concentration. The concentration dependence of $G(-\text{RNO})$ is again that which one would

(6) (a) H. A. Mahlman and G. K. Schweitzer, *J. Inorg. Nucl. Chem.*, **5**, 213 (1958); (b) J. T. Allan, *J. Phys. Chem.*, **68**, 2697 (1964).

(7) H. A. Schwarz, *ibid.*, **66**, 255 (1962).

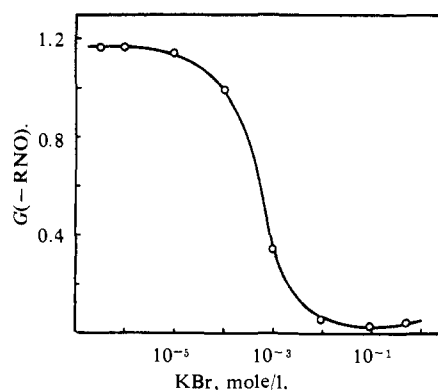
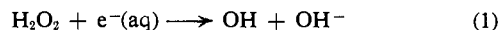


Figure 3. Effect of Br^- on $G(-\text{RNO})$ at pH 9; RNO = $5 \times 10^{-5} M$.

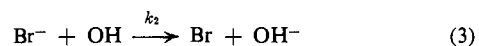
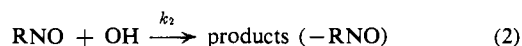
expect from the competition of acetone with RNO for OH radicals.

Another very efficient hydrated electron scavenger, Cd^{2+} ion,⁸ at $10^{-3} M$ concentration had no effect on $G(-\text{RNO})$ at pH 6.0. Thus three different types of scavengers competing with dissolved oxygen for hydrated electrons did not influence the initial $G(-\text{RNO})$.

This and other experimental evidence indicate that RNO as measured at 440 m μ is not bleached by O_2^- or HO_2 radicals. It may be assumed that hydrated electron reacting with O_2 or with other scavengers would give intermediates attacking the RNO chromophoric group. If this were true, the addition of specific OH radical scavengers (Br^- , I^-) should not reduce $G(-\text{RNO})$ to zero or in any case to less than 1 or 2% of the yield in the pure system. On the other hand, the addition of H_2O_2 which is a good hydrated electron scavenger⁵ at low concentrations increased the OH yield and thus also increased $G(-\text{RNO})$ owing to the reaction.



In order to study the OH radical reaction with RNO, competition studies were carried out at pH 9 with compounds known to react efficiently with OH radicals. Chosen were such species as bromide,⁹ iodide,¹⁰ 2-propanol,¹¹ methanol,¹¹ etc. Figure 3 shows a plot of $G(-\text{RNO})$ vs. $\log(\text{Br}^-)$. These preliminary experiments were carried out with unpurified RNO, while all other results were obtained with the twice recrystallized compound. It should be noted that $G(-\text{RNO})$ drops to values which are nearly zero at $(\text{Br}^-) = 0.1 M$, thus indicating a nearly complete competition for the species bleaching the chromophoric group of RNO. The competition kinetics for each of these species were studied by following $G(-\text{RNO})$. For example, if the reactions are simple competition for OH radicals as given in (2) and (3)



(8) E. J. Hart, *Science*, **146**, 19 (1964).

(9) M. Burton and K. C. Kurien, *J. Phys. Chem.*, **63**, 899 (1959).

(10) C. B. Senvar and E. J. Hart, *Proc. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva, 1958*, **29**, 19 (1958).

(11) (a) J. H. Merz and W. A. Waters, *J. Chem. Soc.*, 15 (1949); (b) A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, New York, N. Y., 1960, p. 56.

Table I. Relative Rate Constants for Reactions with OH Radicals and Comparison with Other Published Values

	This work ^a pH 9	Ref. 15 pH 10.5	Ref. 16	Ref. 18	Ref. 17 pH 2.5-10.5	Ref. 12 pH 11	Ref. 13	Ref. 14
RNO	100							
Cl ⁻	<0.01	Very low						
Br ⁻	8.9	9.1	8.8 (88)			6.5		11.7
I ⁻	114	<i>114^b</i>					114 ^c	
CN ⁻	36							
Fe(CN) ₆ ⁴⁻	100	102	134		<i>100^b</i>		(194)	100 ^d
N ₂ ⁻	86							
NO ₂ ⁻	65		161	33		130		
AsO ₂ ⁻	60.7							
(NH ₂) ₂ CO	<0.01							
HCOO ⁻	32.0	29.8	8.2 ^e	3.2 ^e	25.6			
CH ₃ COO ⁻	0.70	0.53					0.15 ^f	
C ₂ O ₄ ²⁻	0.067							
CH ₃ OH	8.6	8.2					5.4	
C ₂ H ₅ OH	14.6	13.5	<i>14.6^b</i>	<i>14.6^b</i>	11.6	<i>14.6^b</i>	8.2	
(CH ₃) ₂ CHOH	17.0			11.4			19.8	
(CH ₂ OH) ₂ CHOH	16.4					21.5		
Salicylate	75.2	48.5						
Uracil	54.2							

^a The values reported in this column have deviations of up to ±5% except for Fe(CN)₆⁴⁻ and C₂O₄²⁻, which have errors of ±15 and ±12%, respectively. ^b Relative values are standardized by setting one of the relative rate constants (italicized) of other authors equal to one of the values in the first column. ^c Absolute value of 1 × 10¹⁰ M⁻¹ sec.⁻¹ for the reaction I⁻ + OH taken as 114. ^d Absolute value of 1.07 × 10¹⁰ M⁻¹ sec.⁻¹ for the reaction Fe(CN)₆⁴⁻ + OH taken as 100. ^e HCOOH. ^f CH₃·COOH.

then it is easily shown that

$$\frac{1}{G(-RNO)} = \frac{1}{G(OH)} \left[1 + \frac{k_3(\text{Br}^-)}{k_2(RNO)} \right] \quad (4)$$

Thus a plot of 1/G(-RNO) vs. (Br⁻)/(RNO) should yield a straight line with slope (1/G(OH)) (k₃/k₂). In Figure 4 is shown a plot of the initial part of the data from separate experiments with recrystallized RNO.

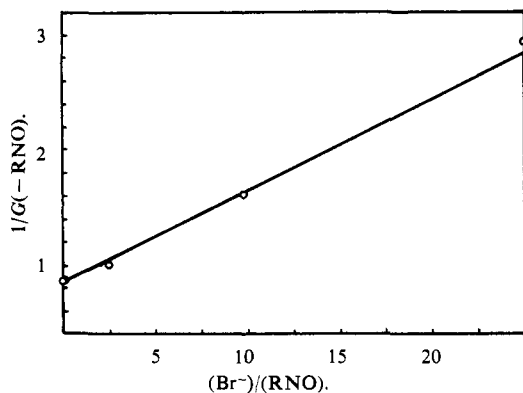


Figure 4. Test of simple competition for OH radicals between RNO and Br⁻ (eq. 4) at pH 9; RNO = 5 × 10⁻⁶ M.

Competition kinetics similar to the air-saturated aqueous Br⁻-RNO system were obtained with I⁻, NO₂⁻, CH₃OH, C₂H₅OH, (CH₃)₂CHOH, and other compounds. Studies of some compounds yielded simple competition kinetics at low concentrations with deviations occurring at higher concentrations. Illustrative examples of the curves obtained are shown in Figures 5 through 8. Thus from the slopes of curves similar to Figures 4, 6, and 8, rate constants of reaction with OH radicals may be obtained. In Table I are shown some

of the relative rate constants obtained in this manner. For purposes of comparison some other relative rate constants calculated from the work of other authors are included in this table. The results show good general agreement with other published values from pulsed electron studies¹²⁻¹⁴ as well as from competition kinetic studies.¹⁵⁻¹⁸

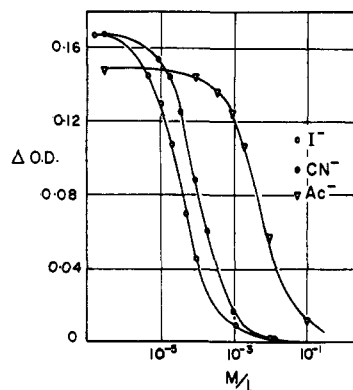


Figure 5. Effect of various ions in optical density change of irradiated RNO solutions at pH 9. ΔO.D. represents the difference in optical density between blanks and 3-min. irradiated samples; RNO = 4 × 10⁻⁶ M; dose rate, 7.4-8.5 × 10¹⁶ e.v. ml.⁻¹ min.⁻¹.

There is still some disagreement in values for NO₂⁻ and to a smaller extent with some other species which may be the result of different pH values used by different authors.

- (12) G. E. Adams and J. W. Boag, *Proc. Chem. Soc.*, 112 (1964).
- (13) J. K. Thomas, *Trans. Faraday Soc.*, 61, 702 (1965).
- (14) J. Rabani, private communication.
- (15) R. W. Matthews and D. F. Sangster, *J. Phys. Chem.*, in press.
- (16) A. O. Allen, *Radiation Res. Suppl.*, 4, 54 (1964).
- (17) J. Rabani and G. Stein, *Trans. Faraday Soc.*, 58, 2150 (1962).
- (18) C. Ferradini, *Advan. Inorg. Chem. Radiochem.*, 3, 171 (1961).

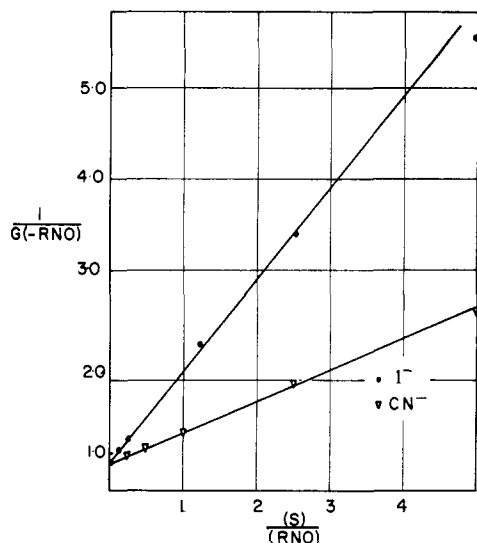


Figure 6. Test of simple competition for OH radicals between RNO and I^- and CN^- , respectively (pH 9); $RNO = 4 \times 10^{-5} M$.

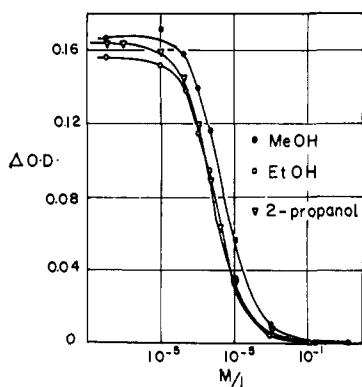


Figure 7. Effect of various alcohols on optical density change of irradiated RNO solutions at pH 9. $\Delta O.D.$ represents the difference in optical density between blanks and 3-min. irradiated samples; $RNO = 4 \times 10^{-5} M$; dose rate, $7.4-8.5 \times 10^{16}$ e.v. $ml^{-1} min^{-1}$.

It may be seen from the Table I that RNO is a very efficient OH radical scavenger and its rate constant is about the same as for ferrocyanide or iodide. This implies that the $RNO + OH$ reaction is diffusion controlled (or nearly so) and that the absolute value for the rate constant would be $\sim 1 \times 10^{10} M^{-1} sec^{-1}$, since the recent values for ferrocyanide^{13,14} and iodide¹³ are reported as $1 \times 10^{10} M^{-1} sec^{-1}$ or higher.

In order to test further the hypothesis that the RNO chromophore was destroyed only by reaction with OH radicals, the photolysis of aqueous air-saturated H_2O_2 -RNO solutions was investigated. Solutions $4 \times 10^{-5} M$ in RNO with H_2O_2 concentrations in the range of 10^{-4} to $10^{-3} M$ were photolyzed with ultraviolet light. Such a system with H_2O_2 up to $2-3 \times 10^{-3} M$ is stable for at least several hours in the absence of ultraviolet light. RNO solutions without H_2O_2 were found to be relatively stable toward this radiation but H_2O_2 is known¹⁹ to dissociate into only OH radicals. By keep-

(19) J. H. Baxendale and J. A. Wilson, *Trans. Faraday Soc.*, 53, 344 (1957).

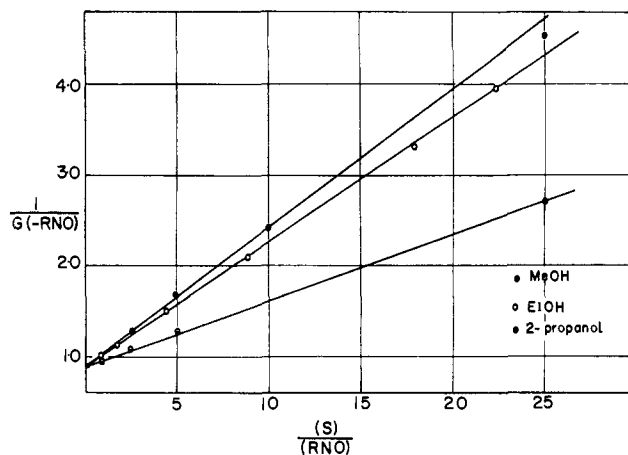


Figure 8. Test of simple competition for OH radicals between RNO and various alcohols (pH 9); $RNO = 4 \times 10^{-5} M$. Upper line, MeOH; middle line, EtOH; lower line, 2-propanol.

ing H_2O_2 at low concentrations, it was possible to avoid secondary attack of OH radicals on H_2O_2 and made possible direct attack of the OH on RNO. Photolytic competition studies were then performed on several systems and relative rate constants identical within experimental error with those obtained in the radiolytic studies were found. Thus in the photolytic experiments where OH radicals were presumably the only reactive intermediates formed, the kinetics were found to be the same as those in the more complex radiolytic experiments where other intermediates in addition to OH are formed.

From the above experimental data we conclude that the bleaching of the RNO chromophoric group at pH 9 is a reaction in the radiolysis of aqueous air-saturated RNO solutions which is specific for OH radicals.

The advantages of this method for such relative rate constant measurements are several. Its high sensitivity stems from the high molar extinction coefficient of RNO. Since the reaction of RNO with OH radicals is diffusion controlled, possible interference due to more complex kinetics is greatly reduced because of the low RNO concentrations employed. The system is rather stable and very reproducible and measurements are taken in visible part of the spectrum ($440 m\mu$). The method is simple, fast, and accurate and all work is done with air-saturated solutions. It appears that oxygen serves to scavenge $e^-(aq)$ and H atoms thus preventing a chromophore-destroying attack on RNO by these species.

The behavior of the system at low pH has been shown²⁰ to be different from that reported above for pH 9 in that $G(-RNO)$ in plots similar to Figure 7 does not fall to zero at high competitor concentration, but tends to level off at a nonzero value. This "residual" yield has been shown²⁰ to be a function of pH and is being further investigated. The products and mechanism of the radiolysis of aqueous RNO solutions is also currently being studied in this laboratory. The determination of relative rate constants for inorganic and organic compounds is also in progress.

(20) I. Kraljic and C. N. Trumbore, paper presented at 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30-Sept. 4, 1964.