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# Rate Constants for Hydrogen Abstraction Reactions of $\text{NO}_3$ in Aqueous Solution

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## Abstract

Rate constants have been measured by pulse radiolysis for the reactions of the  $\text{NO}_3$  radical with five cyclic ethers and a series of alcohols. Rate constants ranged from  $3.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for deuterated methanol to  $1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for tetrahydrofuran. The rate constants for the reactions of  $\text{NO}_3$  with the alcohols 1-propanol to 1-heptanol were found to be linearly dependent on the number of  $\text{CH}_2$  groups with a group reactivity of  $6.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

## Introduction

In previous work from this laboratory, rate constants were reported for reactions of the  $\text{NO}_3$  radical with a number of organic and inorganic reactants [1]. This radical was found to react quite rapidly by electron transfer, somewhat less rapidly by addition to carbon-carbon double bonds, and more slowly by hydrogen abstraction. We have now extended the study of hydrogen abstraction by  $\text{NO}_3$  to a series of alcohols and cyclic ethers. The reactions of  $\text{NO}_3$  in the aqueous phase are of particular interest since the kinetics of this radical has been investigated thoroughly in the gas phase and we can compare those results with the aqueous phase results. The only other radicals for which there are extensive studies in both phases are the hydroxyl radical [2,3] and the hydrogen atom [3,4]. Although the rate constants for hydrogen abstraction by the hydroxyl radical appear to be similar in the gas and aqueous phases, there appears to be less similarity for the reactions of hydrogen atoms.

This investigation was prompted also by the observation that the rate constant for the reaction of  $\text{SO}_4^{\cdot -}$  with primary alcohols does not simply increase linearly with the number of carbons, but increases more rapidly above 1-hexanol [5]. This observation is in contrast to the results observed for the reaction of OH with the same alcohols in the gas phase, where the rate constant was observed to increase more slowly for the higher alcohols [6]. Also, we found that the rate constant for the reaction of  $\text{SO}_4^{\cdot -}$  with *p*-dioxane is lower than for the reaction with tetrahydrofuran [7]. Assuming the C—H bonds  $\alpha$  to the ether linkage are weaker than normal secondary C—H bonds, the reverse order of reactivity would be expected. In

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this work, we want to determine if this phenomenon persists for the uncharged radical  $\text{NO}_3$ .

### Experimental

Nitric acid was ACS reagent grade from Fisher.<sup>a</sup> Tetrahydrofuran and *p*-dioxane were from Eastman and the tetrahydrofuran was vacuum distilled before use; tetrahydropyran was from Aldrich, trimethylene oxide from ICN pharmaceuticals, and *m*-dioxane from Pfaltz and Bauer. Ethanol was USP grade from Mallinckrodt, 1-butanol was from Fisher, and 2-methyl-1-propanol was from Eastman. All other alcohols were the best available from Aldrich.

Stock solutions of 6 M  $\text{HNO}_3$  were prepared fresh daily and allowed to cool to room temperature before use. Solutions were flowed under air through a 2-cm quartz reaction cell and pulse irradiated by a Febetron 705 accelerator which delivered 2 MeV electrons at doses of about 3 krad/pulse. The solution was illuminated by a 300-W xenon arc lamp and the radicals monitored spectrophotometrically at 640 nm. The decay in optical absorption was recorded on a Tektronix 7612D transient recorder, the decay curves processed on a PDP 11/34 minicomputer or a PC Designs CV-386 microcomputer, and first-order rate constants derived by linear least-squares analysis. Second-order rate constants were derived from linear plots of the observed decay rate vs. the concentration of added solutes (see Fig. 1). The standard deviation of the slope was typically better than 10%. All measurements were carried out at room temperature, ca. 22°C.

### Results and Discussion

The  $\text{NO}_3$  radical was produced by the pulse radiolysis of 6 M  $\text{HNO}_3$  solutions. In our previous work [1], we found that the spectrum of the transient produced in this way matched that reported for  $\text{NO}_3$  produced in the flash photolysis of ceric nitrate solutions [8,9] and was similar to the gas-phase spectrum of this radical. From the maximum absorption at 600 nm, and assuming an absorptivity [9] of  $1000 \text{ M}^{-1} \text{ cm}^{-1}$ , we calculate that under our typical operating conditions the  $\text{NO}_3$  radical concentration was about 6–12  $\mu\text{M}$ . In addition to  $\text{NO}_3$ , other free radicals are generated during the pulse radiolysis of nitric acid. These contribute to the decay of  $\text{NO}_3$  (particularly  $\text{NO}_2$ ) in the absence of added reactant and result in the intercepts observed in the second-order plots (Fig. 1).

Rate constants measured for the reactions of  $\text{NO}_3$  with a series of saturated organic reactants are listed in Table I. Included for comparison are rate constants for the reactions of  $\text{SO}_4^-$  with the same reactants. The logarithms of these rate constants are compared in Figure 2. On average, the  $\text{NO}_3$  radical reacts about 50 times slower than  $\text{SO}_4^-$ . The significant deu-

<sup>a</sup> Certain commercial equipment, instruments, or materials are identified in this article in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

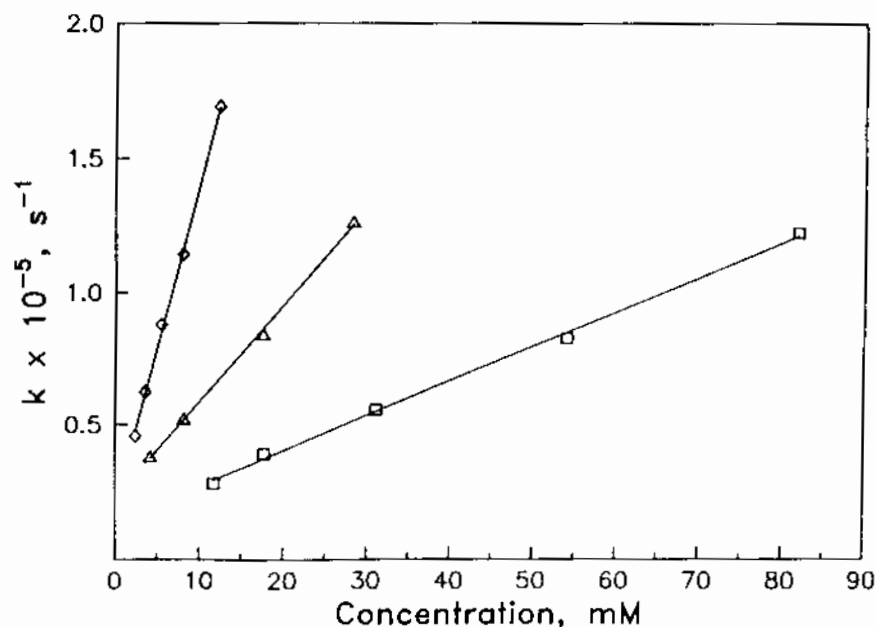
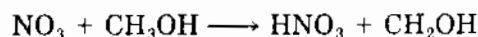


Figure 1. First-order rate constant as a function of concentration.  $\square$ -*p*-Dioxane;  $\Delta$ -1-Heptanol; and  $\diamond$ -Tetrahydrofuran.

terium isotope effect for both  $\text{NO}_3$  and  $\text{SO}_4^-$  (Table I) confirms that these reactions are hydrogen abstraction. The rate constants measured in this work for methanol and ethanol are slightly lower than reported in ref. [1], probably due to insufficient cooling in the earlier work. (We expect these reactions to have a strong temperature dependence.) We were quite surprised to find the rate constant for the reaction of  $\text{NO}_3$  with ethanol equal to that for 1-propanol and, as shown in Figure 3, above a line extrapolated from the higher alcohols. Therefore, we also determined the rate constant for this reaction with a sample of ethanol which had been vacuum distilled and obtained the same result. We have no explanation for this comparatively high rate constant for ethanol, but note that the gas-phase reaction of  $\text{O}^3\text{P}$  with 1-propanol has been reported to be slower than its reaction with ethanol [10].

The thermochemistry of the  $\text{NO}_3$  radical in aqueous solutions has not been established. In the gas phase, the reaction



has been calculated [11] to be exothermic by  $24.7 \text{ kJ mol}^{-1}$ . Therefore, even at our highest methanol concentration (0.5 M), the reaction would be expected to go to completion.

A possible complication in these studies involves the production of reactive radicals by reaction of other primary radiolytic products (most notably OH) with the alcohols and the subsequent reaction of these products with  $\text{NO}_3$ . This, however, is unlikely due to the low concentration of primary radicals produced in the pulse (10–20  $\mu\text{M}$  at the dose used). This problem

TABLE I. Rate constants for some hydrogen-abstraction reactions of  $\text{NO}_3$  and  $\text{SO}_4^-$ .

Reactant	$k, \text{M}^{-1} \text{s}^{-1}$	
	$\text{NO}_3$	$\text{SO}_4^-$ <sup>a</sup>
Methanol	$1.8 \times 10^5$	$1.0 \times 10^7$
Methanol-d <sub>4</sub>	$3.5 \times 10^4$	$3.7 \times 10^6$
Ethanol	$1.1 \times 10^6$	$4.3 \times 10^7$
1-Propanol	$1.1 \times 10^6$	$5.9 \times 10^7$
1-Butanol	$1.9 \times 10^6$	$8.0 \times 10^7$
1-Pentanol	$2.4 \times 10^6$	$1.3 \times 10^8$
1-Hexanol	$3.3 \times 10^6$	$1.6 \times 10^8$
1-Heptanol	$3.6 \times 10^6$	$2.5 \times 10^8$
1-Octanol	$5.8 \times 10^6$	$3.4 \times 10^8$
2-Propanol	$2.4 \times 10^{6b}$	$8.3 \times 10^7$
2-Methyl-1-propanol	$1.6 \times 10^6$	$1.3 \times 10^8$
Cyclopentanol	$3.2 \times 10^6$	$2.8 \times 10^8$
Trimethylene oxide	$1.5 \times 10^6$	
Tetrahydrofuran	$1.1 \times 10^7$	$2.8 \times 10^8$
Tetrahydropyran	$4.9 \times 10^6$	
m-Dioxane	$7.7 \times 10^5$	
p-Dioxane	$1.3 \times 10^6$	$7.3 \times 10^7$

<sup>a</sup>Rate constants for alcohols from ref. [2], for ethers, from Ref. [4].<sup>b</sup>From ref. [1].

would be expected to manifest itself as a second-order component to the  $\text{NO}_3$  decay or a deviation from linearity in the second-order plots (Fig. 1). In both cases, the expected kinetic behavior was observed.

Since the  $\text{NO}_3$  reactions are so slow, we have not been able to investigate the range of reactions we investigated for  $\text{SO}_4^-$ . In particular, we were not able to derive a value for the reactivity of primary or tertiary C—H bonds. The reactivity of  $\text{NO}_3$  toward secondary C—H bonds ( $\geq \beta$ ) can be estimated from the increase in rate constant for primary alcohols with the number of  $\text{CH}_2$  groups. For 1-propanol through 1-heptanol, a linear increase was observed and a rate constant of  $3.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for secondary C—H abstraction was derived (Fig. 3). Similar to our observations for  $\text{SO}_4^-$ , where 1-heptanol and 1-octanol reacted faster than the extrapolated line predicted, the point for 1-octanol is higher than the calculated line.

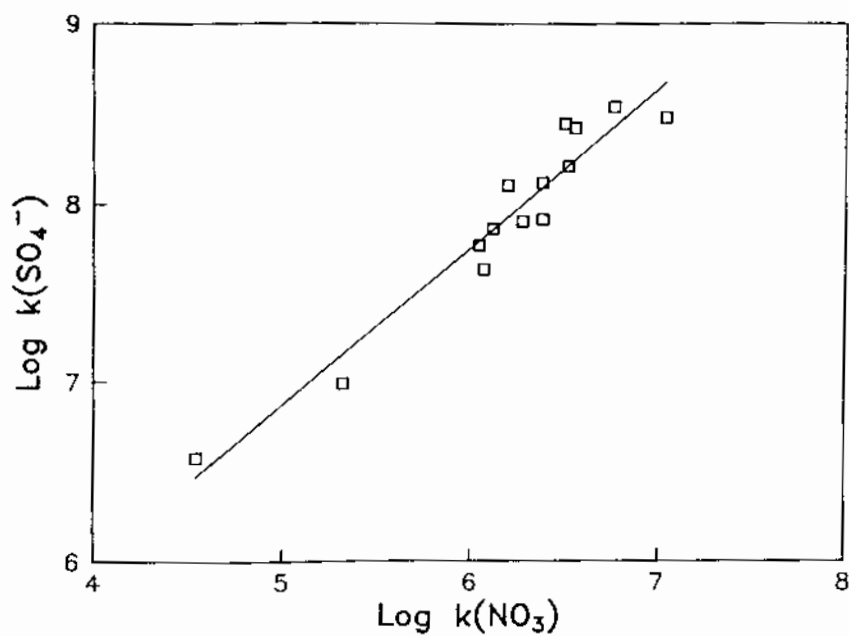


Figure 2. Correlation of the logarithm of the rate constants for hydrogen-abstraction reactions of the  $\text{SO}_4^{\bullet-}$  and the  $\text{NO}_3$  radical. Rate constant in units of  $\text{M}^{-1} \text{s}^{-1}$ .

Again, this is contrary to the observations on the reactivity of OH towards alcohols in the gas phase.

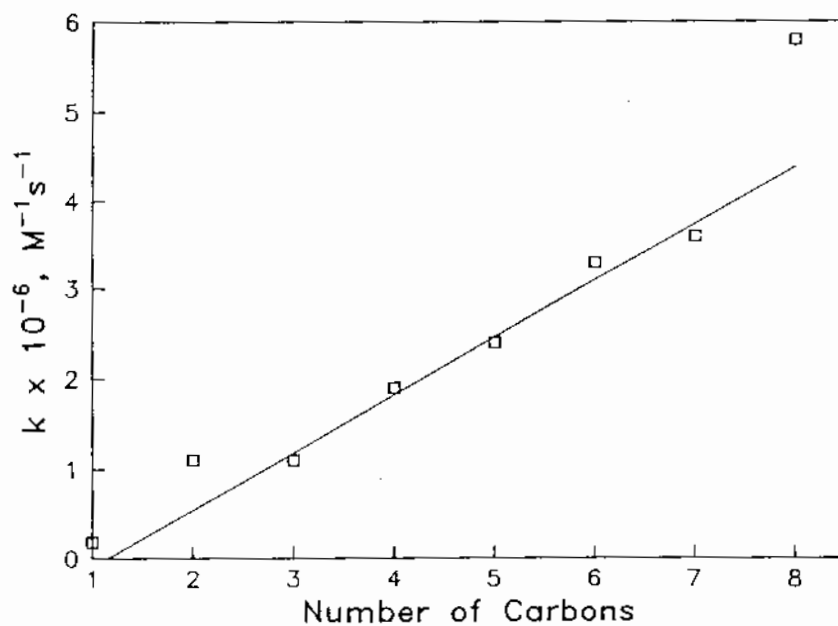


Figure 3. Rate constant for the reactions of  $\text{NO}_3$  with primary alcohols as a function of the number of carbon atoms.

TABLE II. Rate constants for reactions of free radicals with tetrahydrofuran and *p*-dioxane.

Radical	$k, \text{M}^{-1}\text{s}^{-1}$		
	Tetrahydrofuran	<i>p</i> -Dioxane	Ratio
$\text{NO}_3$	$1.1 \times 10^7$	$1.3 \times 10^6$	8.5
$\text{H}^\bullet$	$7.2 \times 10^7$	$1.2 \times 10^7$	6
$\text{O}^3\text{P}(\text{gas})^b$	$2.3 \times 10^8$	$4.1 \times 10^7$	5.6
$\text{SO}_4^\bullet$	$2.8 \times 10^8$	$7.3 \times 10^7$	3.8
$\text{OH}^\bullet$	$4.0 \times 10^9$	$3.1 \times 10^9$	1.3
$\text{OH}(\text{gas})^d$	$9.7 \times 10^9$	$6.6 \times 10^9$	1.5

<sup>a</sup> P. Neta, R. W. Fessenden, and R. H. Schuler, *J. Phys. Chem.*, **75**, 1654 (1971).

<sup>b</sup> R. Liu, P. Dagaut, R. E. Huie, and M. J. Kurylo, in preparation.

<sup>c</sup> J. Eibenberger, Ph.D. Thesis, Vienna University, Vienna, Austria, 1980.

<sup>d</sup> Ref. [16].

A report has appeared very recently on the reactions of  $\text{NO}_3$  with some alcohols in water and acetonitrile [12]. The  $\text{NO}_3$  radical was produced by the flash photolysis of  $(\text{NH}_3)_2[\text{Ce}(\text{NO}_3)_6]$  and was monitored by absorption spectroscopy. The rate constants reported for the reactions of  $\text{NO}_3$  in water with ethanol and 2-propanol ( $1.2$  and  $2.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) are essentially identical to ours. The rate constants reported for the reactions of  $\text{NO}_3$  with methanol and deuterated methanol ( $3.1$  and  $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ), however, are greater than those we measured. The ratio of the rate constants for nondeuterated to deuterated methanol in their work is about 2, while we find the ratio to be 5. In the same article, Ito et al. [12], report that the reactivity of  $\text{NO}_3$  towards alcohols in acetonitrile is about ten times greater than it is in water; the ratio of the rate constants for nondeuterated to deuterated methanol in that medium is 3.4. (In both cases, the reactivity of  $\text{NO}_3$  towards methanol deuterated only on the oxygen was the same as toward totally undeuterated methanol, indicating that abstraction takes place only from the C—H bond.) In general, we expect the selectivity of an abstraction reaction, and therefore the deuterium isotope effect, to increase as the reactivity decreases. So we would expect the ratio to be greater in water, where the rate constants are lower, than in acetonitrile, in agreement with our observation. We note that the  $\text{SO}_4^\bullet$  radical (Table I), which is more reactive than  $\text{NO}_3$  and therefore less selective, gives a lower value for this ratio [5], and an even lower ratio is given by the  $\text{OH}$  radical [3].

The higher reactivity of  $\text{NO}_3$  in acetonitrile than in water is of considerable interest. In the electron-transfer reaction between  $\text{CCl}_3\text{O}_2$  and a substituted phenol (trolox), the opposite was observed: the rate constant increased as the dielectric constant of the solvent increased and was fur-

ther enhanced by the ability of the solvent to participate in proton transfer [13]. Similarly, the hydrogen abstraction reaction of the *tert*-butoxyl radical with a polyunsaturated fatty acid was found to proceed ten times faster in water than in a nonpolar solvent [14].

There also has been a recent determination of the rate constant for the gas-phase reaction of  $\text{NO}_3$  with methanol [11]. A rate constant (calculated for 22°C) of  $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  was reported, slightly below our value of  $1.8 \times 10^5$  in water but much less than the value of  $2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  measured in acetonitrile. Theoretical calculations suggest that hydrogen abstraction reactions should be faster in inert solvents than in the gas phase [15]. The experimental results, then, suggest that there is a strong interaction of the  $\text{NO}_3$  radical with water which slows the reaction. The similarity in the rate constants between the gas and aqueous phases is probably fortuitous.

The reactivity of tetrahydrofuran and *p*-dioxane towards  $\text{NO}_3$  and a series of other radicals is compared in Table II. In all cases, tetrahydrofuran is more reactive than *p*-dioxane, while the ratio of reactivities decreases as the reactivity increases. In some very recent work, the reactivity of a number of cyclic ethers towards OH has been determined in the gas phase [16]. Of the cyclic ethers investigated, tetrahydrofuran was the most reactive, with tetrahydropyran (with one more  $\text{CH}_2$  group) and trimethylene oxide (with one less  $\text{CH}_2$  group) both less reactive. For  $\text{NO}_3$ , we see the same order of reactivity, but magnified by the greater selectivity of this radical. OH is also less reactive towards *m*-dioxane than *p*-dioxane, as is  $\text{NO}_3$ . For OH, the 4- and 5-member ring ethers (trimethylene oxide and tetrahydrofuran) were more reactive per  $\text{CH}_2$  group than the larger ethers and both were less reactive than predicted from the reactivity of OH towards linear aliphatic ethers.

It is clear, then, that  $\text{NO}_3$  and gas-phase OH exhibit the same general reactivity pattern in their reactions with cyclic ethers. For *p*-dioxane and tetrahydrofuran, at least, this reactivity pattern is true for a number of atoms and free radicals. The reason for the order of reactivity of these cyclic ethers, however, is not at all clear. It appears that the  $\alpha \text{ C-H}$  bonds in tetrahydrofuran are much weaker than the equivalent bonds in any of the other cyclic ethers. It seems unlikely that this is due to ring strain, since both trimethylene oxide, with one less carbon than tetrahydrofuran, and tetrahydropyran, with one more carbon, are less reactive. Additional ether linkages, as in *p*-dioxane and *m*-dioxane, appear to make the compound even less reactive.

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