## Radiolytic Reductions and Oxidations in Dimethyl Sulfoxide Solutions. Solvent Effects on Reactivity of Halogen Atom Complexes

#### M. Kumar and P. Neta\*

Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 (Received: October 14, 1991; In Final Form: December 6, 1991)

Radiolysis of dimethyl sulfoxide (DMSO) solutions containing various additives was used to achieve clean one-electron reduction or oxidation of solutes. Pulse radiolysis of benzoquinone in DMSO solutions containing acetone and triethylamine permitted conversion of all primary radicals into reducing species. The total yield of reduction in the  $\gamma$ -radiolysis of methyl viologen solutions was found to be 0.37 µmol/J. In the pulse radiolysis of TMPD and triphenylamine in aerated DMSO containing LiCl and/or CCl<sub>4</sub>, all the primary radicals were converted into oxidizing species and gave a maximum yield of 0.39  $\mu$ mol/J. In the latter systems, oxidation was partly by halogen atom complexes. The reactivity of complexes of DMSO (DMSO-Cl, DMSO-Br) and of halide ions (Br2<sup>+,</sup> I2<sup>+)</sup> was examined for several organic compounds. DMSO-Cl oxidizes chlorpromazine, triphenylamine, and zinc porphyrin with rate constants of the order of  $10^7 - 10^8 M^{-1} s^{-1}$ , and the rates increase upon addition of  $CH_2Cl_2$  as well as upon addition of water and formamide. DMSO-Cl also reacts with olefins by addition of Cl to the double bond; the rate constants increase upon increasing the electron-donating properties of the substituents on the double bond. The rate constants for oxidation of chlorpromazine by  $Br_2^{*-}$  and  $I_2^{*-}$  increase by more than 2 orders of magnitude upon changing the solvent from DMSO gradually to water. The change was less with acetonitrile/water mixtures, and the difference is probably due to differences in ion solvation.

#### Introduction

The radiolysis of dimethyl sulfoxide (DMSO) results in the formation of solvated electrons and positive ions.<sup>1</sup>

> DMSO ----- DMSO + + e (1)

The solvated electrons absorb in the infrared and are formed with a yield of  $\sim 0.18 \ \mu \text{mol}/\text{J}$  (G  $\approx 1.8 \ \text{electrons}/100 \ \text{eV}$ ), as determined from their reactions with  $N_2O$ , biphenyl, or anthracene. The positive ions absorb near 600 nm, and their yield was estimated from their reactions with N,N,N',N'-tetramethyl-pphenylenediamine (TMPD) or Br-. To achieve high radiolytic yields of either reduction or exidation of a solute in DMSO, it is advantageous to convert all the primary species into reducing or oxidizing radicals. This will be important in the use of DMSO as solvent, e.g., for radiolytic redox reactions of metalloporphyrins<sup>2,3</sup> or for dosimetry with radiochromic dyes.<sup>4</sup>

To obtain clean reduction, we attempted to use several organic compounds that may react with the DMSO\*+ to yield a reducing radical. A good compound for this purpose was found to be triethylamine. To obtain clean oxidation, we utilized electron scavengers that result in the formation of oxidizing species. One of the best scavengers is CCl<sub>4</sub>, which is reduced by e<sup>-</sup> to CCl<sub>3</sub>. and Cl<sup>-</sup> and in the presence of oxygen it forms CCl<sub>3</sub>O<sub>2</sub><sup>•</sup>, a known oxidizing species.

In the course of these studies we examined the reactivity of several oxidizing radicals produced in DMSO solutions in the presence of organic and inorganic halides, i.e., complexes of the type DMSO-X and  $X_2^{-5,6}$  We found a strong effect of solvent composition on the reactivity of these species produced in

 $DMSO/CH_2Cl_2$ ,  $DMSO/H_2O$ , and other mixtures.

#### Experimental Section<sup>7</sup>

The organic compounds were of the purest grade commercially available and were generally used as received. Chlorpromazine hydrochloride (CPZ), 3-methylindole, and methyl viologen (MV<sup>2+</sup>) chloride were from Sigma, zinc tetratolylporphyrin (ZnTTP) was from Midcentury Chemical Co., benzoquinone was from Fisher, and the alkenes from Eastman and Aldrich. Triphenylamine (TPA) was from Aldrich and was further purified by recrystallization from ethyl acetate/ethanol. N, N, N', N'-Tetramethyl-p-phenylenediamine (TMPD) was also from Aldrich and was purified by sublimation. Triethylamine (TEA) and tert-butylamine were vacuum distilled. Methyl iodide from Aldrich was purified by passing through activated neutral alumina. Dibromomethane was a Fluka puriss reagent. Dimethyl sulfoxide (DMSO) and allyl alcohol were Aldrich Gold Label. Dichloromethane, 2-propanol, acetone, acetonitrile, cyclohexane, carbon tetrachloride, and the inorganic compounds were analytical grade reagents from Mallinckrodt. Water was purified with a Millipore Super-O system.

Fresh solutions were prepared before each experiment and were irradiated either under air or after bubbling with Ar or  $N_2O$ .  $\gamma$ -Radiolysis was carried out in a Gammacell 220 <sup>60</sup>Co source with a dose rate of 93 Gy/min. Pulse radiolysis was carried out with the apparatus described before,<sup>8</sup> which utilizes 50-ns pulses of 2-MeV electrons from a Febetron Model 705 accelerator. The dose per pulse was between 10 and 40 Gy in most experiments, as determined by dosimetry with N<sub>2</sub>O-saturated aqueous KSCN solutions.<sup>9</sup> The laser flash photolysis system consisted of a Lambda Physik EMG 201 MSC excimer laser, utilizing KrF for 248 nm, with a pulse duration of 20-40 ns and pulse energies of 150-500 mJ. The kinetic spectrophotometric detection system was similar in both setups.<sup>8,10</sup> The signals were digitized with a Tektronix 7612D transient recorder and analyzed with a PC-Design GV-386 computer. All experiments were carried out at room temperature,  $22 \pm 2$  °C.

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<sup>(7)</sup> The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for the purpose

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#### **Results and Discussion**

Pulse radiolysis experiments with DMSO solutions containing various solutes were carried out to optimize the yields of reduced or oxidized species and to measure the rate constants for certain reactions. Radiolytic yields of stable products were determined by  $\gamma$ -radiolysis experiments.

Reduction of Quinone and Methyl Viologen. Pulse radiolysis of benzoquinone (Q) in deoxygenated DMSO solutions resulted in the formation of the semiquinone radical (reaction 2), which

$$\mathbf{Q} + \mathbf{e}^{-} \to \mathbf{Q}^{*-} \tag{2}$$

exhibited an absorption spectrum with peaks at 430 and 450 nm, with neary equal molar absorptivities, a minor dip ( $\sim 10\%$ ) at 440 nm, and a strong absorption below 340 nm. The DMSO<sup>++</sup> (reaction 1) may lower the yield by reacting with  $e^-$  (by geminate ion recombination) and may lower the lifetime of Q<sup>-</sup> by oxidizing it. The first effect may be overcome to some extent by increasing the concentration of Q. Since [Q] may be limited by experimental constraints, we utilized acetone as an efficient electron scavenger to convert e<sup>-</sup> into the longer-lived and more selectively reducing (CH<sub>3</sub>)<sub>2</sub>CO<sup>--</sup> radical.

$$(CH_3)_2CO + e^- \rightarrow (CH_3)_2CO^{--}$$
(3)

$$(CH_3)_2CO^{\bullet-} + Q \rightarrow (CH_3)_2CO + Q^{\bullet-}$$
(4)

Addition of 0.95 M acetone to 0.8 mM Q increased the absorbance of Q<sup>--</sup> at 450 nm from 0.056 to 0.073. To convert DMSO<sup>++</sup> into reducing species we utilized triethylamine (TEA), which is known to form the reducing radical  $CH_3CHN(C_2H_5)_2$  (2-PrOH was not effective for this purpose). Addition of 1% (0.07 M) TEA to 0.89 mM Q increased the absorbance of Q<sup>•-</sup> to 0.098 (5% TEA gave a slightly higher increase but 0.1% TEA had only a minor effect). When both acetone and TEA were present, an absorbance of 0.117 was observed. The absorbance was also dependent on [Q]; a plateau value was reached at [Q] = 3-4 mM. Since the molar absorptivity,  $\epsilon$ , of Q<sup>--</sup> in DMSO is unknown, we can only estimate the reduction yield by assuming  $\epsilon = 7300 \text{ M}^{-1} \text{ cm}^{-1}$  as in aqueous solutions.<sup>11</sup> By using thiocyanate dosimetry,<sup>9</sup> and correcting for differences in solvent electron densities, we obtain a value of 0.42  $\mu$ mol/J, somewhat higher than expected on the basis of the primary yields reported previously.<sup>1</sup> To obtain a more accurate reduction yield we have used  $MV^{2+}$  in  $\gamma$ -radiolysis experiments.

Methyl viologen (MV<sup>2+</sup>) undergoes one-electron reduction to form a stable radical (MV\*+) which exhibits strong absorptions around 400 and 600 nm. In DMSO, the second peak was found to be at 610 nm and to have a molar absorptivity of  $\epsilon_{610} = 1.1$  $\times 10^4$  M<sup>-1</sup> cm<sup>-1</sup> (determined by reduction with sodium dithionite). We have utilized this absorption to determine the initial yield of reduction in the  $\gamma$ -radiolysis of deaerated DMSO solutions from plots of absorbance vs irradiation time. With 1.3 mM MV<sup>2+</sup>, 0.95 M acetone, and 0.07 M TEA, a reduction yield of 0.37  $\mu$ mol/J was observed, in good agreement with the previous reports that the yield of the electron and the radical cation are each 0.18  $\mu$ mol/J.<sup>1</sup>

Oxidation of Triphenylamine, Porphyrin, and TMPD. The radical cation DMSO<sup>++</sup> has been shown to oxidize Br<sup>-</sup> ions, TMPD, and other compounds. The lifetime of DMSO<sup>++</sup>, however, is relatively short so that high solute concentrations may be necessary to achieve full scavenging. In cases where high concentrations are not practical, such as with porphyrins, it may be advantageous to convert the primary cation into a longer-lived oxidizing radical. This may be achieved for example by converting DMSO<sup>+</sup> into DMSO-Cl or into Br<sub>2</sub><sup>--</sup> as discussed below.

To prevent the back-reduction of the product with e, it is simple to use aerated solutions, where  $O_2$  will scavenge  $e^-$  to form the weakly reactive  $O_2^-$ . Converting  $e^-$  into OH (or  $O^-$  in aprotic

solvent) by reaction with  $N_2O$ , as is done in aqueous solutions, does not necessarily result in greater yield of oxidizing species since OH (or O<sup>-</sup>) reacts with DMSO to form an adduct which rapidly decomposes to give methyl radicals.<sup>12</sup> Only in acidic solutions, where the DMSO-OH adduct protonates to form an oxidizing species, DMSO- $OH_2^{+,13}$  can this reaction be useful. Therefore, we used CCl<sub>4</sub> and other halogenated hydrocarbons, which are known to undergo reductive dehalogenation and to form peroxyl radicals in the presence of oxygen.

$$CCl_4 + e^- \rightarrow CCl_3^{\bullet} + Cl^-$$
 (5)

$$\operatorname{CCl}_3^{\bullet} + \operatorname{O}_2 \to \operatorname{CCl}_3\operatorname{O}_2^{\bullet}$$
 (6)

These peroxyl radicals have been shown to oxidize a variety of organic compounds fairly rapidly.<sup>14</sup> Thus, solutes in DMSO may be oxidized with a yield equal to the sum of the yields of  $e^-$  and DMSO++.

Pulse radiolysis of triphenylamine in DMSO, with and without other solutes, gave the characteristic spectrum of the TPA\*+ radical cation with a peak at 670 nm.<sup>15,16</sup> Similarly, ZnTTP formed the ZnTTP<sup>++</sup> radical cation with a peak at 630 nm. The rate constants for these oxidation reactions are discussed below. To determine the total yield of oxidation we used TMPD, since this compound is oxidized to a stable radical cation whose molar absorptivity is  $1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  in various solvents.<sup>17</sup> The yield of TMPD<sup>++</sup> in the pulse radiolysis of aerated DMSO solutions containing 5% CCl<sub>4</sub> increased with concentration and reached a plateau of 0.39  $\mu$ mol/J at [TMPD] = 3-5 mM, in good agreement with the sum of the reported primary yields of  $e^-$  and DMSO<sup>+1</sup>.<sup>1</sup>  $\gamma$ -Radiolysis of similar solutions gave a slightly higher yield, 0.42  $\mu$ mol/J.<sup>18</sup> These results suggest that in the use of DMSO as solvent for dosimetry with radiochromic dyes,<sup>4</sup> the yield of the dye product and thus the sensitivity of the dosimeter may be increased by a factor of  $\sim 3$  with the use of organic halides as additives.

Formation of Halogen Atom Complexes. DMSO has been shown to form complexes with Cl and Br atoms. The DMSO-Cl complex may be formed by reaction of DMSO<sup>+</sup> with Cl<sup>-</sup> or reaction of DMSO with Cl atoms.<sup>5,6</sup> The contributions of the two paths in the radiolysis of DMSO/CCl4 mixtures have been shown to depend on solvent composition, i.e., on whether the energy is deposited in DMSO to form the cation or in CCl<sub>4</sub> to form the Cl atom. The path through DMSO<sup>+</sup> + Cl<sup>-</sup> becomes more quantitative upon addition of Cl<sup>-</sup> to the solution, to supplement the small yield of  $Cl^-$  from the reaction of  $e^-$  with  $CCl_4$ . (This path has been demonstrated recently in aqueous solutions as well.<sup>13b</sup> The path through Cl atoms is efficient with CCl4 but becomes less so with other chlorinated hydrocarbons when H-abstraction by Cl atoms may occur.

We have recorded the absorption spectra after pulse radiolysis of DMSO containing various concentrations of LiCl or CCl4 and found in all cases the 400-nm peak of DMSO-Cl. The absorbance increased with LiCl concentration and reached a plateau at  $\sim 0.1$ M salt. We have obtained the same complex also by laser flash photolysis (at 248 nm) of DMSO in CH<sub>2</sub>Cl<sub>2</sub> (0.085 M DMSO gave the maximum yield under these conditions). The same complex has been observed previously in the flash photolysis (266 nm) of CCl<sub>4</sub> (0.02 M) in DMSO.<sup>19</sup> In the latter case, the 266-nm light was absorbed by CCl<sub>4</sub>, probably preassociated with DMSO,<sup>19</sup>

<sup>(11)</sup> Adams, G. E.; Michael, B. D. Trans. Faraday Soc. 1967, 63, 1171. However, the absorption spectrum of the semiquinone in water is slightly different from that we find in DMSO, possibly due to different interactions between the radical anion and the polar solvent molecules or due to complexation between them.

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<sup>(18)</sup> However,  $\gamma$ -radiolysis of TMPD in DMSO with 5% CH<sub>2</sub>Cl<sub>2</sub> gave only 0.29 µmol/J TMPD\*+, unexpectedly lower than that found with CCl4.

TABLE I: Rate Constants for Reactions of DMSO-Cl with Several Compounds under Various Conditions<sup>a</sup>

solution composition	CPZ	ZnTTP	TPA	t-BuNH <sub>2</sub>	1,2-DMCH	
 DMSO, 0.1 M LiCl	$8.4 \times 10^{7}$	9.6 × 10 <sup>7</sup>			$2.3 \times 10^{6}$	
$DMSO/CCl_4 = 9/1$	$6.8 \times 10^{7 b}$	$1.4 \times 10^{8 b}$	$1.3 \times 10^{7}$		$3.2 \times 10^{6}$	
$DMSO/CH_2Cl_2 = 20/1, 0.1 M LiCl$	$9.4 \times 10^{7}$	$1.5 \times 10^{8}$ c	$1.2 \times 10^{7}$	$3.4 \times 10^{6}$	$3.7 \times 10^{6}$	
$DMSO/CH_2Cl_2 = 1/1, 0.1 M LiCl$	$2.2 \times 10^{8}$	$2.7 \times 10^{8}$	$2.3 \times 10^{7}$		$9.4 \times 10^{6}$	
$DMSO/CH_{2}Cl_{2} = 1/20$	$4.8 \times 10^{8}$	$1.1 \times 10^{9}$	$7.0 \times 10^{7}$	$5.1 \times 10^{6}$	$4.2 \times 10^{7}$	
$DMSO/H_{2}O = 9/1, 0.1 M LiCl$	$1.3 \times 10^{8}$				$8.9 \times 10^{6}$	
$DMSO/HCONH_2 = 9/1, 0.1 M LiCl$	$2.2 \times 10^{8}$					

<sup>a</sup> Determined by pulse radiolysis (given in  $M^{-1} s^{-1}$ ), accurate generally to ±15% for the higher values and to ±20% for the lower values. <sup>b</sup> The rate constant may be affected by contribution from the reaction of CCl<sub>3</sub>OO<sup>•</sup> with the compounds. The contribution was shown to be eliminated by the exclusion of O<sub>2</sub> to prevent formation of the peroxyl radical. This effect is unimportant in the case of CH<sub>2</sub>Cl<sub>2</sub> because of the much lower reactivity of its peroxyl radical. <sup>c</sup> Determined in DMSO/CH<sub>2</sub>Cl<sub>2</sub> = 9/1.

to form the Cl atom directly complexed with the solvent. On the other hand, in our experiments using  $CH_2Cl_2$  as solvent, the 248-nm light is absorbed by the DMSO to result probably in excitation. The excited state may react with  $CH_2Cl_2$  to form either Cl atom or DMSO<sup>++</sup> + Cl<sup>-</sup>, which subsequently form the DMSO-Cl complex.

The reaction of DMSO<sup>+</sup> with Br<sup>-</sup> also has been found to lead to formation of DMSO·Br as is evident from the spectrum of the product with  $\lambda_{max}$  430 nm, observed in the pulse radiolysis of NaBr (0.2 mM) in DMSO, which is identical with the spectrum obtained by reaction of Br atoms with DMSO. At high [Br<sup>-</sup>] (0.1 M), however, the spectrum shifts to  $\lambda_{max}$  360 nm, indicating formation of Br<sub>2</sub><sup>--</sup>, as suggested before.<sup>5</sup>

$$DMSO^{+} + Br^{-} \rightarrow DMSO \cdot Br$$
 (7)

$$DMSO \cdot Br + Br \rightarrow DMSO + Br_2^{-}$$
 (8)

In the case of I<sup>-</sup> and SCN<sup>-</sup>, no complexes with DMSO were evident even at low halide concentrations, and only  $I_2^{*-}$  ( $\lambda_{max}$  380 nm) and (SCN)<sub>2</sub><sup>\*-</sup> ( $\lambda_{max}$  480 nm) were observed, in agreement with the previous report.<sup>5</sup> We were unable to observe the formation of Cl<sub>2</sub><sup>\*-</sup> even at high [Cl<sup>-</sup>] (1 M) and even after addition of acid (0.1 M HCl). These results suggest that the DMSO-X complex may be viewed as a complex of the halogen atom with neutral DMSO in the case of Br but is probably more polar in the case of Cl, i.e., has a greater contribution from the ionic structure DMSO<sup>+</sup>·Cl<sup>-</sup>. Because of the high electron affinity of Cl, this complex does not transfer a Cl atom to Cl<sup>-</sup> ion to give Cl<sub>2</sub><sup>\*-</sup>.

**Reactions of Halogen Atom Complexes.** The results described above enable us to use these systems to examine the reactivities of DMSO·Cl, DMSO·Br,  $Br_2^{\bullet-}$ , and  $I_2^{\bullet-}$  with various reactants that are soluble in DMSO or in DMSO mixtures with several other solvents. The second-order rate constants were determined by following the decay of the radical absorption at the appropriate wavelength (400, 430, 360, and 380 nm, respectively) as a function of added solute concentration. In the case of CPZ, ZnTTP, and TPA, the formation of the product radical absorptions at 525, 630, and 670 nm, respectively, was followed since these absorptions are more intense and give more accurate results and since the decay of the initial radicals cannot be followed accurately in the presence of these compounds or their products. The rate constants, summarized in Tables I–III, show strong solvent effects on reactivity.

Table I gives the rate constants for reaction of DMSO-Cl with CPZ and ZnTTP, which are oxidized to their radical cations, with TPA and t-BuNH<sub>2</sub>, which form the nitrogen-centered radicals either by oxidation or by hydrogen abstraction, and with an olefin that may react by addition or H-abstraction. The DMSO-Cl was produced in three systems: in DMSO/LiCl, by reaction of DMSO<sup>++</sup> + Cl<sup>-</sup>, and in DMSO/CCl<sub>4</sub> and DMSO/CH<sub>2</sub>Cl<sub>2</sub>/LiCl, by reactions of both DMSO<sup>++</sup> + Cl<sup>-</sup> and DMSO + Cl<sup>+</sup>. For each compound examined, the rate constants in these three systems are found to be similar (within experimental error). However, when the ratio DMSO/CH<sub>2</sub>Cl<sub>2</sub> is changed from 20/1 to 1/1 and

TABLE II: Rate Constants for Reactions of DMSO-Cl with Alkenes

compound	kª	σ* <sup>b</sup>
1,2-dimethylcyclohexene	$4.2 \times 10^7  (pr)^c$	-0.24
	$3.8 \times 10^7  (lp)^d$	
2-methyl-3-ethyl-2-pentene	$2.4 \times 10^7  (lp)^d$	-0.20
2,3-dimethyl-2-butene	$2.1 \times 10^7  (pr)^c$	0.00
-	$1.9 \times 10^7  (lp)^d$	
3-ethyl-2-pentene	$1.1 \times 10^7  (lp)^d$	0.29
	$9.0 \times 10^{6}  (pr)^{c}$	
3-methyl-2-pentene	$1.2 \times 10^7  (lp)^d$	0.39
	$7.9 \times 10^{6}  (pr)^{c}$	
2-ethyl-1-butene	$4.4 \times 10^6  (lp)^d$	0.78
cyclohexene	$2.6 \times 10^{6} (\text{pr})^{e}$	0.74
1-hexene	$6.5 \times 10^5  (lp)^d$	1.40

<sup>a</sup> Rate constants in  $M^{-1} s^{-1}$ , accurate generally to  $\pm 15-20\%$ , except for the low rate constant determined for 1-hexene, which is accurate to  $\pm 35\%$ . <sup>b</sup> Taft's  $\sigma^*$  substituent constants from ref 21, calculated for each double bond as the sum of the individual  $\sigma^*$  values of the substituents, using the following: H, +0.49; CH<sub>3</sub>, 0.00; C<sub>2</sub>H<sub>5</sub>, -0.10; *n*-Bu, -0.13. For the cyclic alkenes we calculated the values by assuming two open ends. <sup>c</sup> Determined by pulse radiolysis in solutions containing 5% DMSO in CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup> Determined by 248-nm laser flash photolysis in solutions containing 0.085 M DMSO in CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Determined by pulse radiolysis in solutions containing 1% DMSO in CH<sub>2</sub>Cl<sub>2</sub>, ref 6.

TABLE III: Rate Constants for Oxidation by  $Br_2^{-}$  and  $I_2^{-}$  Radicals in Aqueous DMSO Solutions

reaction	H <sub>2</sub> O/DMSO (v/v) <sup>a</sup>	k, <sup>b</sup> M <sup>-1</sup> s <sup>-1</sup>
$Br_2^{*-}$ + chlorpromazine	100/0	$7.6 \times 10^{9}$
2 1	90/10	$3.5 \times 10^{9}$
	80/20	$2.9 \times 10^{9}$
	50/50	$1.1 \times 10^{9}$
	20/80	$1.1 \times 10^{8}$
	10⁄90	$3.3 \times 10^{7}$
	4/96	$1.3 \times 10^{7}$
	0/100	$\leq 1 \times 10^{7}$
Br <sub>3</sub> •- + ZnTTP	0/100	≤10 <sup>7</sup>
Br <sub>2</sub> <sup>•-</sup> + 3-methylindole	80/20	$7.3 \times 10^{8}$
2	50/50	$2.2 \times 10^{8}$
	20/80	$8.9 \times 10^{6}$
$I_2^{*-}$ + chlorpromazine	100/0	$2.0 \times 10^{9}$ c
2	90/10	$1.3 \times 10^{9}$
	80/20	$7.4 \times 10^{8}$
	50/50	$4.8 \times 10^{7}$
	20/80	$\leq 1 \times 10^{7}$

<sup>a</sup> The solutions also contained 0.1 M NaBr or NaI and varying concentrations of the reductants and were pulse irradiated under air. <sup>b</sup> Accurate to  $\pm 15-20\%$ . <sup>c</sup> From ref 26.

then 1/20, the rate constant, k, for each compound is found to increase by a factor of ~2 and a factor of 5–10, respectively. Since the nature of the reacting species, DMSO-Cl, apparently does not change with solvent composition, as no change is observed in its absorption spectrum, there must be a strong solvent effect on the rate of reaction. In fact, a linear correlation is observed (Figure 1) between log k and the mole fraction of  $CH_2Cl_2$  (or DMSO). The mechanism of these reactions probably involves the reversible transfer of the Cl atom from DMSO-Cl to the compound (A) as a first step, as suggested before for Br atom complexes.<sup>15</sup>

$$DMSO \cdot Cl + A \rightleftharpoons DMSO + A \cdot Cl$$
(9)

<sup>(19)</sup> Sumiyoshi, T.; Watanabe, K.; Syogen, S.; Kawasaki, M.; Katayama, M. Bull. Chem. Soc. Jpn. 1990, 63, 1584.



Figure 1. Dependence of the rate constants, k, for reaction of DMSO-Cl with chlorpromazine ( $\blacktriangle$ ) and with 1,2-dimethylcyclohexene ( $\blacklozenge$ ) on solvent composition (mole fraction of DMSO in the DMSO/CH<sub>2</sub>Cl<sub>2</sub> solvent).

Subsequently, A-Cl may give the final products by elimination of  $Cl^-$  or HCl.

$$A \cdot Cl \rightarrow A^{*+} + Cl^-$$
 (or  $A(-H)^* + HCl$ ) (10)

When the ratio of DMSO/CH<sub>2</sub>Cl<sub>2</sub> is decreased, the overall rate constant may be changed by two opposing effects. On one hand, since  $k_{obs}$  depends on  $K_9$  and inversely on [DMSO], decreasing [DMSO] shifts equilibrium 9 to the right and accelerates the formation of products. This effect appears to be the dominant one upon changing the DMSO/CH<sub>2</sub>Cl<sub>2</sub> ratio. On the other hand, when reaction 10 involves ionic species, it may be accelerated by increasing solvent polarity, i.e., with increasing [DMSO]. This effect is more clearly seen upon replacing the CCl<sub>4</sub> in the DMSO/CCl<sub>4</sub> = 9/1 mixture with the highly polar water or formamide, showing an increase in rate constant with CPZ by factors of 2 and 4, respectively.

The rate constants for reaction of DMSO-Cl with alkenes were measured by pulse radiolysis as described above and also by laser flash photolysis (Table II). In the latter type of experiment, solutions containing 0.085 M DMSO in CH<sub>2</sub>Cl<sub>2</sub> were photolyzed with 248-nm laser pulse. Light absorption by DMSO results in the formation of the DMSO-Cl complex. The rate constants (k)determined by the two techniques are identical, within experimental error, and vary over 2 orders of magnitude, depending strongly on the structure of the alkene. The observed dependence of k on structure indicates that the reaction is predominantly via addition and not via H-abstraction from allylic or other aliphatic C-H bonds.<sup>20</sup> A good correlation is found (Figure 2) between log k and the sum of the Taft's  $\sigma^*$  substituent constants<sup>21</sup> for the substituents on the double bond. This correlation is similar to that observed before for the reactions of the alkenes with  $C_4F_9OO^{\bullet}$ radicals<sup>22</sup> and indicates that the mechanism of reaction involves mainly electrophilic addition to the double bond. The selectivity of DMSO-Cl is somewhat lower than that of  $C_4F_9OO^4$ , the slope  $\rho^*$  is found from Figure 2 to be -1.0 as compared with -1.4 measured for the peroxyl radical. Correlation between  $\log k$  and the ionization potential of the olefin was less extensive, because the values of the ionization potentials are not known for all the olefins studied. The six known values give a more scattered fit of the data but indicate clearly that the rate constant increases



Figure 2. Correlation between log k for reactions of DMSO-Cl in  $CH_2Cl_2$  solutions with various alkenes and the sum of Taft's  $\sigma^*$  substituent constants for the groups attached to the double bond.



Figure 3. Dependence of the rate constants, k, for reactions of  $X_2^{\bullet-}$  with chlorpromazine in water/DMSO or water/CH<sub>3</sub>CN solutions on mole fraction of organic component for  $Br_2^{\bullet-}$  in water/DMSO ( $\bullet$ ),  $I_2^{\bullet-}$  in water/DMSO ( $\bullet$ ),  $I_2^{\bullet-}$  in water/CH<sub>3</sub>CN ( $\blacksquare$ ).

when the ionization potential decreases. The same trend has been observed recently in the reactions of  $Cl_2^{--}$  with unsaturated alcohols.<sup>23</sup>

Similar experiments were also attempted with DMSO-Br, but the results were less reliable and are not reported here. Some of the more reliable data were obtained for three olefins and indicated somewhat higher rate constants for DMSO-Br as compared with DMSO-Cl, probably indicating that the DMSO-Br complex is less stable<sup>24</sup> so that equilibrium 9 is shifted to the right as compared with the case of DMSO-Cl. The lower stability of DMSO-Br and its subsequent conversion to  $Br_2^{--}$  in the presence of low  $Br^$ concentrations may be one of the main reasons for the difficulty in obtaining reliable rate constants.

The rate constants for oxidation of chlorpromazine and 3methylindole by  $Br_2^{\bullet-}$  and  $I_2^{\bullet-}$  were measured in various  $H_2O/DMSO$  mixtures (Table III). The yield of CPZ<sup>++</sup> decreased only slightly upon adding 10–20% DMSO to the aqueous solution despite the fact that under these conditions all the OH radicals produced in the radiolysis of water are scavenged by DMSO rather than by the halide ion.<sup>25</sup> Due to the slightly acidic conditions

<sup>(20)</sup> On the basis of the rate constant for the least reactive alkene, we can estimate that the rate of H-abstraction from allylic and CH<sub>2</sub> positions is  $\ll 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . This estimate indicates that DMSO-Cl is much less reactive than the *π*-complex benzene-Cl which reacts with alkanes at least 2 orders of magnitude more rapidly. See, e.g.: Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lusztyk, J.; Scaiano, J. C. J. Am. Chem. Soc. **1985**, 107, 5464.

<sup>(21)</sup> Taft, R. W., Jr. In Steric Effects in Organic Chemistry; Newman, M. S., Ed.; Wiley: New York, 1956; p 619.

<sup>(22)</sup> Nahor, G. S.; Neta, P. Int. J. Chem. Kinet. 1991, 23, 941.

<sup>(23)</sup> Padmaja, S.; Neta, P.; Huie, R. E. J. Phys. Chem., following paper in this issue.

<sup>(24)</sup> The lower stability of DMSO-Br as compared with DMSO-Cl has been discussed recently (ref 13b) in terms of the different stabilities of the three-electron bonds between the sulfur and the halogen. A stability constant of 560  $M^{-1}$  has been determined for DMSO-Cl in acidic aqueous solutions.

TABLE IV: Rate Constants for Reaction of  $Br_2^{-}$  with Chlorpromazine in Water/Acetonitrile Solutions

H <sub>2</sub> O/CH <sub>3</sub> CN	k, M <sup>-1</sup> s <sup>-1</sup>	H <sub>2</sub> O/CH <sub>3</sub> CN	k, M <sup>-1</sup> s <sup>-1</sup>	
100/0	7.6 × 10 <sup>9</sup>	20/80	$6.2 \times 10^{8}$	
80/20	$3.5 \times 10^{9}$	10/90	$3.4 \times 10^{8}$	
50/50	$1.6 \times 10^{9}$			

caused by the use of CPZ·HCl, the DMSO·OH apparently forms the protonated form, DMSO·OH<sub>2</sub><sup>+</sup>,<sup>13</sup> which can oxidize Br<sup>-</sup> and I<sup>-</sup>, and thus the yields remain in the same range ( $\pm 25\%$ ).

The rate constants measured for the reactions of  $Br_2^{\bullet-}$  and  $I_2^{\bullet-}$  depend strongly on solvent composition. The value of k for  $Br_2^{\bullet-}$ 

$$Br_2^{-} + CPZ \rightarrow 2Br^- + CPZ^{+}$$
 (11)

+ CPZ decreases from  $7.6 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> in 100% H<sub>2</sub>O (nearly identical with the reported value)<sup>26</sup> to  $\leq 10^7$  M<sup>-1</sup> s<sup>-1</sup> in 100% DMSO. The rate constants for Br<sub>2</sub><sup>•-</sup> + 3-methylindole and for I<sub>2</sub><sup>•-</sup> + CPZ also decrease in the same fashion. Very good linear correlation is found (Figure 3) between log k and the mole fraction of DMSO. The slope of the line is larger for the slower I<sub>2</sub><sup>•-</sup> reaction than for the faster Br<sub>2</sub><sup>•-</sup> reaction. The magnitude of the slope appears too high to be accounted for by simple solvent polarity effects. In fact, the same reaction of Br<sub>2</sub><sup>•-</sup> + CPZ when examined in various water/acetonitrile mixtures (Table IV) also gives a similar correlation with the mole fraction of acetonitrile (39) and DMSO (45) are not too different. For solvents of high dielectric constants such as these, the effect of the medium di-

(25) For rate constants of hydroxyl radicals and hydrated electrons with various compounds, see compilation by: Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. J. Phys. Chem. Ref. Data 1988, 17, 513.

electric constant on the reaction is of minor importance compared with specific solvation effects.<sup>27</sup> Reaction 11 becomes slower when the solvent is changed from water, which is a good solvator for both cations and anions, to acetonitrile, which is a poorer solvator for both ions. However, DMSO has a stronger effect because it is a good solvator for the cations and very poor solvator for the anions,<sup>28</sup> which lowers the driving force for reaction 11.

#### Conclusion

Deoxygenated DMSO solutions containing small amounts of acetone and triethylamine (1%) are a good medium for clean radiolytic one-electron reduction of many solutes. Aerated DMSO solutions containing small amounts of CCl4 (or other halogenated hydrocarbons), with or without LiCl, provide a medium for radiolytic oxidation. The yield of reduction and oxidation depends somewhat on concentration and approaches 0.4  $\mu$ mol/J, the sum of the primary yields of DMSO<sup>++</sup> and e<sup>-</sup> produced by the radiolysis. This overall yield of reducing and oxidizing species in DMSO is about one-third lower than the value in aqueous solutions. Thus, a wide variety of compounds and reactions may be studied conveniently in DMSO when they cannot be studied in aqueous solutions. However, DMSO exerts a strong effect on the rate constants of various reactions, partly due to its high solvent polarity as compared with many other organic solvents and, more importantly, due to its ability to effectively solvate cations but not anions. Thus, the reactivity of Br2\* decreases tremendously upon going from water to DMSO. Furthermore, DMSO forms complexes with Cl and Br atoms which exhibit reactivities different from Cl<sub>2</sub><sup>--</sup> and Br<sub>2</sub><sup>--</sup> observed in water and other solvents.

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# Rate Constants and Temperature Effects for Reactions of $Cl_2^-$ with Unsaturated Alcohols and Hydrocarbons in Aqueous and Acetonitrile/Water Solutions

### S. Padmaja, P. Neta, and R. E. Huie\*

Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 (Received: November 18, 1991; In Final Form: January 8, 1992)

Absolute rate constants for reactions of the dichlorine radical anion,  $Cl_2^{\bullet-}$ , with unsaturated alcohols and hydrocarbons have been measured at various temperatures. The alcohol reactions were measured in aqueous solutions and the hydrocarbon reactions in 1:1 aqueous acetonitrile (ACN) solutions. The rate constants for two alcohols and one hydrocarbon were also examined as a function of solvent composition. The room temperature rate constants varied between  $10^6$  and  $10^9 M^{-1} s^{-1}$ . The pre-exponential factors, A, were about  $(1-5) \times 10^9 M^{-1} s^{-1}$  for the alcohols in aqueous solutions and about  $(0.1-1) \times 10^9 M^{-1} s^{-1}$  for the hydrocarbons in aqueous ACN solutions. The activation energies,  $E_a$ , varied considerably, between 4 and 12 kJ mol<sup>-1</sup> for the alcohols and between 2 and 8 kJ mol<sup>-1</sup> for the hydrocarbons. The rate constants,  $k_{298}$ , decrease with increasing ionization potential (IP) of the unsaturated compound, in agreement with an electrophilic addition mechanism. The activation energies for the unsaturated alcohols decrease when the IP decreases from 9.7 to 9.1 eV but appear to level off at lower IP. Most alkenes studied had IP < 9.1 eV and showed little change in  $E_a$ . Upon addition of ACN to the aqueous solution, the values of log  $k_{298}$  decreased linearly by more than 1 order of magnitude with increasing ACN mole fraction. This decrease appears to result from a combination of changes in the activation energy and in the pre-exponential factor, in combination with changes in solvation of Cl<sup>-</sup>, which will affect the energetics of the reactions as well.

#### Introduction

Although rate constants have been measured for a large number of reactions of inorganic radicals in aqueous solution,<sup>1</sup> until recently few measurements have been made at other than room temperature. In studies of the temperature dependence of electrontransfer reactions of inorganic radicals with organic<sup>2</sup> and inorganic<sup>3</sup> reactants, the reactivity has been found to correlate more with the pre-exponential factor in the Arrhenius equation than with

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