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Photochemical Reactions of Uranyl Ions with Organic Compounds. V. Effects of Temperature and Solvent on the Photooxidation of Alcohols

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A comparative study of the photokinetic behaviors of aliphatic alcohols and related substrates was made for the photooxidation with uranyl ions. Ethylene glycol, glucose, sucrose and some other substrates showed abnormal results compared to a series of simple aliphatic alcohols: the photoredox quantum yields ϕ for the former substrates decreased with substrate concentration (at their higher concentrations) and temperature rise, in contrast to simple aliphatic alcohols. In aqueous acetone solution ϕ increased with the increase in acetone content, the reaction constant ρ^* being more negative than in aqueous solution. In 40% aqueous acetone solution the ϕ values for simple aliphatic alcohols varied in a complicated way with temperature. The abnormal results were interpreted in terms of the relative importance of physical quenching competing with the primary chemical process.

As regards the mechanism of the photooxidation of some aliphatic alcohols by uranyl ions, the initial stage was assumed to be the α-hydrogen abstraction (one-equivalent redox) *via* bimolecular collision of the excited uranyl ion with the substrates, followed by the two disproportionation reactions of the primary intermediates.[1,2]

However, in the course of the photokinetic investigations, we observed that some alcohols, such as glucose and benzyl alcohol, exhibited abnormal behaviors.

In the present paper the effects of temperature, substrate concentration and solvent on the photokinetics are discussed.

Experimental

Guaranteed reagents were used without purification. 0.02 M uranyl nitrate solution was prepared from a 0.1 M stock solution. The solutions (pH=1) were deaerated by the passage of oxygen-free nitrogen for 20—30 min per 5—15 ml, kept air-tight with liquid paraffin and then exposed to irradiation (mostly 405 and 436 nm) using a suitable combination of glass filters or an interference filter from a 100 or 500 W high pressure mercury lamp. The temperature was controlled with a thermostat.

Methods for actinometry and determination of the photoproducts were the same as those previously described.[1] Since the molar ratio of the products, aldehyde or ketone/uranium(IV), was unity regardless of the conditions,[1] only the formation of the uranium(IV) species was followed for the estimation of the photoredox quantum yield ϕ.

Results and Discussion

Effects of Temperature and Substrate Concentration. The plot of the reciprocal of the photoredox quantum yield $1/\phi$ as a function of the reciprocal of alcohol concentration gave a straight line for the photooxidation of simple aliphatic alcohols by uranyl ions in aqueous acidic media, in agreement with the empirical equation: $1/\phi=\alpha+\beta/[\text{alcohol}]$, where $\alpha=2$ at $\text{pH}\geqq 1$[1] (Fig. 1). The relation seems to hold under some different conditions (temperature and solvent) for *n*-propyl alcohol (Fig. 1). The photoredox reaction of ethyl and three butyl alcohols with uranyl ions has been explained by a mechanism which involves one-equivalent redox reaction between the excited uranyl ions and the substrates *via* bimolecular collision, followed by thermal disproportionation reactions of the primary redox intermediates.[1] The fact that the photoredox quantum

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[1] S. Sakuraba and R. Matsushima, This Bulletin, **43**, 2359 (1970).

[2] R. Matsushima and S. Sakuraba, *J. Amer. Chem. Soc.*, **93**, 5421 (1971).

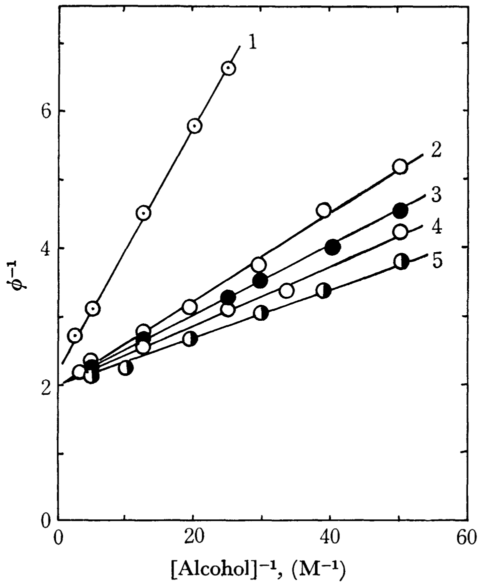


Fig. 1. Plot of ϕ^{-1} *vs.* [alcohol]$^{-1}$ in aqueous acidic solutions (pH=1). 1: methyl, 2: ethyl, 3: *n*-propyl, 4: *n*-butyl, 5: *sec*-butyl alcohol.

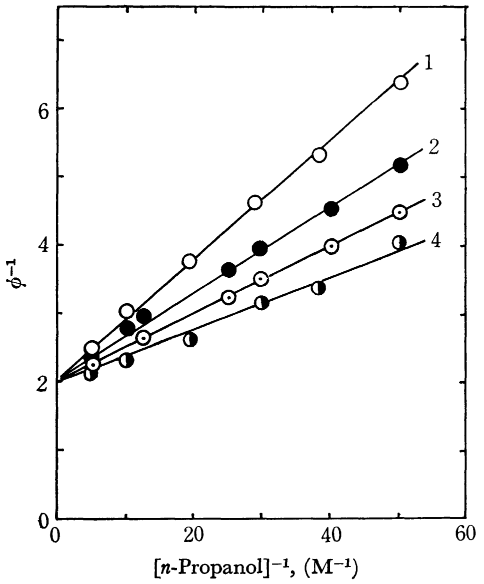


Fig. 2. Plot of ϕ^{-1} *vs.* [*n*-propyl alcohol]$^{-1}$ at different temperatures at pH 1. 1: 3 °C, 2: 10 °C, 3: 20 °C, 4: 20 °C in 40% aqueous acetone.

yield increases with temperature (Fig. 2) might support the bimolecular collision mechanism.

In contrast, the plot $1/\phi$ *vs.* $1/$[substrate] for ethylene glycol, glucose, and sucrose gave no straight line (Fig. 3). This implies that some depression of the photoredox reaction becomes significant with the increase in substrate concentration at higher concentrations (>0.1 M). The photoredox quantum yield decreases with temperature rise for thse substrates, whereas the reverse is the case for simple aliphatic alcohols (Fig. 2). Plots of $\log\phi$ *vs.* $1/T$ for simple aliphatic alcohols are given in Fig. 4. Ethyl, isopropyl, *n*-butyl and isobutyl alcohols gave similar results. Plots for glucose and benzyl alcohol are given in Fig. 5. Qualitatively, the positive apparent activation energies for simple aliphatic

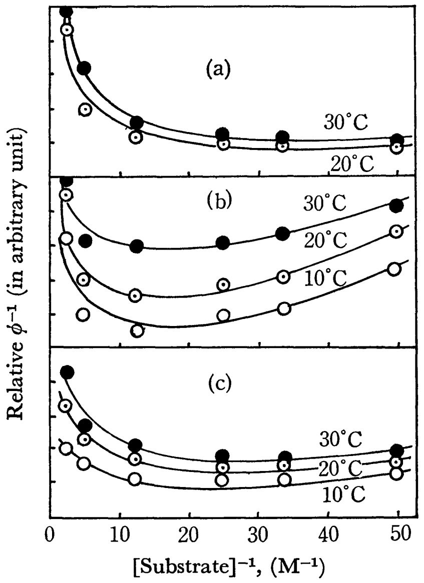


Fig. 3. Plot of relative ϕ^{-1} *vs.* [substrate]$^{-1}$ at different temperatures in aqueous acidic solutions (pH=1)
(a): ethylene glycol, (b): glucose, (c): sucrose.

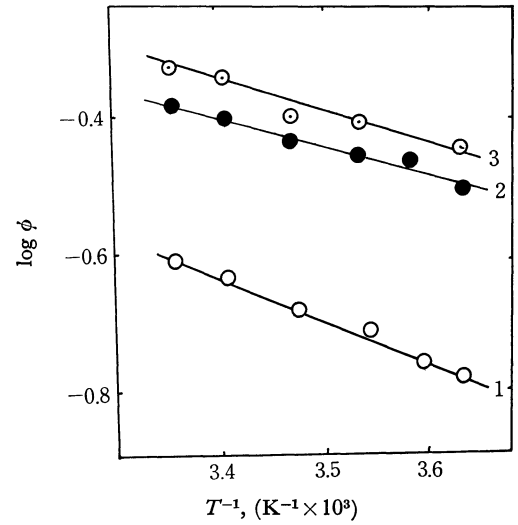


Fig. 4. Plot of log ϕ *vs.* $1/T$. 1: methyl, 2: *n*-propyl, 3: *sec*-butyl alcohol, in 0.1 M. Aqueous acidic medium (pH=1).

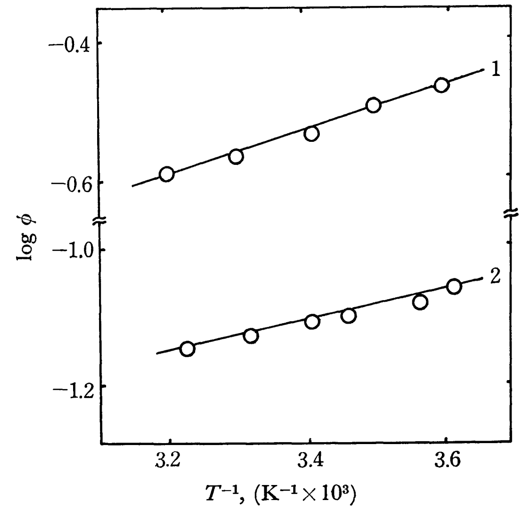


Fig. 5. Plot of log ϕ *vs.* $1/T$ for glucose (1) and benzyl alcohol (2) in aqueous acidic medium (pH=1).

TABLE 1. VARIATION IN THE PHOTOREDOX QUANTUM YIELD WITH ACETONE CONTENT[a)]

Acetone/vol%	ϕ
0	0.38
5	0.43
20	0.44
40	0.45
60	0.46

a) Ethyl alcohol 0.1 M, uranyl ion 0.02 M, pH=1, 20 °C.

alcohols, 2—5 kcal/mol, might support a bimolecular collision mechanism, but not negative apparent activation energies for glucose and benzyl alcohol, −1.5 kcal/mol.

Solvent Effects. Change in the photoredox quantum yield with acetone content is given in Table 1. The increase in ϕ with the acetone content is partly attributable to the increase in the mean lifetime of uranyl fluorescence. The Stern-Volmer plots gave straight lines for most aliphatic alcohols in 40% aqueous acetone as well as in aqueous medium.

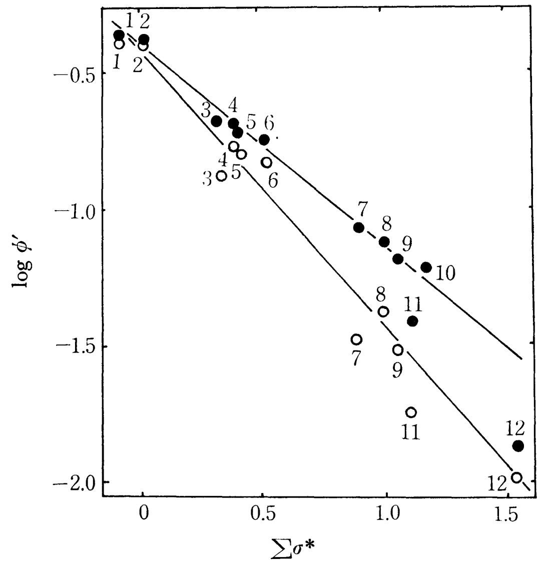


Fig. 6. Plot of log ϕ' *vs.* $\sum\sigma^*$ at pH 1, 20 °C. $\sum\sigma^*=\sigma(R_1)+\sigma^*(R_2)$; $\sigma^*(R_1)$ and $\sigma^*(R_2)$ are Taft σ^*-values of the substituents R_1 and R_2 in R_1R_2CHOH. ϕ' is the photoredox quantum yield divided by the number of the α-hydrogen atoms of each alcohol. 1: *sec*-butyl, 2: isopropyl, 3: isobutyl, 4: *n*-butyl, 5: *n*-propyl, 6: ethyl, 7: 3-chloro-*n*-propyl, 8: methyl, 9: 2-hydroxyethyl, 10: 2-propenyl, 11: benzyl, 12: 2-chloroethyl alcohols; 0.1 M in each alcohol.
○: 40% aqueous acetone, ●: aqueous medium.

Figure 6 shows the polar substituent effect of alcohols on the photoredox quantum yield in 40% aqueous acetone as compared with that in aqueous medium. The ρ^*-values under some different conditions are in the range $-1.4<\rho^*<-0.6$, an indication of a free radical reaction.[3)] The ρ^*-value remains unchanged with the changes in temperature and alcohol concentration, but it changes with the change in the medium (Table 2). This might be attributed to the effect of solvent polarity.

TABLE 2. EFFECTS OF TEMPERATURE, SOLVENT AND ALCOHOL CONCENTRATION ON THE ρ^*-VALUE

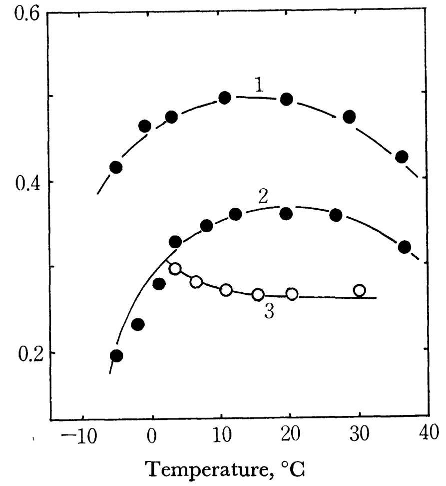
Temperature/°C	Solvent	[Alcohol]/M[a)]	$-\rho^*$
4	water	0.04	0.80
20	water	0.10	0.80
35	water	0.04	0.80
20	40 % acetone	0.06	0.95

a) Alcohols are the same as in Fig. 6.

The Stern-Volmer formula, the linearity of the plot of log ϕ' *vs.* $\sum\sigma^*$, and the range of the ρ^*-value, indicate that the primary process in 40% aqueous acetone is similar to that in aqueous medium, *i.e.*, α-hydrogen abstraction.[1,2)]

On the other hand, plot 4 in Fig. 2 shows a straight line with the intercept of 2 in 40% aqueous acetone medium. The intercept of 2 suggests that the secondary process in this medium is similar to that in aqueous medium, *i.e.*, disproportionation reactions of the primary redox intermediates.[1)]

Thus, it is very likely that the photoredox reaction in aqueous acetone proceeds through a similar mechanism to that in aqueous medium with different efficiency.



Temperature, °C

Fig. 7. Temperature dependence of ϕ in 40% aqueous acetone at pH 1. 1: *n*-butyl alcohol, 2: ethyl alcohol, 3: glucose, 0.1 M in each.

The temperature dependence of the photoredox quantum yield in 40% aqueous acetone is shown in Fig. 7. Ethyl and butyl alcohols show abnormal temperature effect in this medium compared to aqueous medium (Fig. 4). Glucose shows a different dependence.

Discussion on the Abnormal Results. Some authors[4,5)] have postulated a ground state complex as the photosensitive species for the photooxidation of sugars and alcohols by uranyl ions. Multidentate alcohols (ethylene glycol, glucose, and sucrose) would have stronger coor-

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3) a) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963); b) C. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964); c) R. L. Huany and K. H. Lee, *J. Chem. Soc.*, *C*, **1966**, 935. d) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **90**, 4755 (1968); **92**, 1120 (1970).

4) a) L. J. Heidt and K. A. Moon, *ibid.*, **75**, 5803 (1953); b) L. J. Heidt, *ibid.*, **76**, 5962 (1954).

5) a) K. Venkatarao and M. Santappa, *Z. Phys. Chem.* (Frankfurt), **54**, 101 (1967); b) K. Venkatarao and M. Santappa, *Indian J. Chem.*, **5**, 304 (1967).

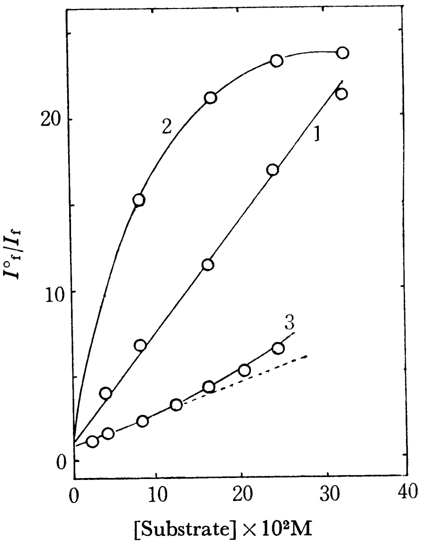

Fig. 8. Typical Stern-Volmer plots for the uranyl fluorescence by alcohols and the related substrates. Uranyl ion: 0.02 F, pH=1 (aqueous medium), 25 °C, λ_{ex}=405 nm, λ_{an}=510 nm.

1: *n*-propyl alcohol, 2: glucose, 3: lactic acid

dination power than unidentate alcohols.[6] The negative apparent activation energies for the multidentate alcohols (Figs. 3 and 5) might be interpreted in terms of the formation of a ground state complex as the photosensitive species in contrast to the positive ones for the unidentate alcohols (Figs. 2 and 4).

If complex formation takes place between the substrates and the uranyl ions, changes in the absorption and/or the fluorescence spectra of the solutions might be expected. The Stern-Volmer plots for the quenching of the uranyl fluorescence by these substrates should give lines concave upward (as is the case for lactic acid, Fig. 8), since the quenching efficiency should increase because of the additional static (intracomplex) quenching process, which is more efficient than a bimolecular collision process.[7] However, the absorption spectra (visible region) and shapes of the fluorescence spectra of uranyl ions in aqueous solution at pH 1 were entirely unchanged by the addition of these substrates in the range of uranyl concentration 0.001—0.1 M. This is in contrast to the fact that even weak complexes with many carboxylic acids show significant spectral changes,[8] though the lack of spectral changes does not always exclude complex formation. The Stern-Volmer plot for glucose gave a line concave downward (the reverse of expectation) as shown in Fig. 8. It seems difficult to explain the decrease in ϕ at higher substrate concentrations (Fig. 3) in terms of complex formation, since increase in substrate concentration should accelerate the formation. Thus, the formation of a ground state complex as the photosensitive species is unlikely and negligible at most.

The relative importance of physical quenching which competes with the primary chemical process might be a possible interpretation of our results. It should be noted that the quenching constants for the multidentate alcohols and phenyl-substituted alcohols are large compared to their photoredox quantum yields.[9] This implies the important role of physical quenching for these substrates, while for simple aliphatic alcohols (physical quenching is small), temperature rise is qualitatively equivalent to the increase in substrate concentration in the sense that the number of effective collisions for the primary chemical act is roughly proportional to substrate concentration and absolute temperature. However, this is not the case for substrates with significant physical quenching efficiencies or for even simple aliphatic alcohols at higher temperature in more complicated media where solute-solvent interaction becomes more sensitive to temperature change. The abnormal temperature dependence of ethyl and butyl alcohols in 40% aqueous acetone (Fig. 7) may be assumed to be the latter case.

For complicated substrates or those for which physical quenching is dominant, effective collision for the chemical process will be restricted, hence the greater part of the primary interaction is apt to fall into physical quenching, giving rise to large quenching constants compared to their photoredox quantum yields. For these substrates the increase in temperature will decrease the viscosity of solutions so as to increase the number of collisions between the reactants, but it will depress the efficient abstraction of α-hydrogen because of the increased steric hindrance (thermal rotations of the bulky groups) of the substrate molecules. It is probable that the increment of the primary chemical act (α-hydrogen abstraction) due to the decreased viscosity (or increased number of collisions) is small compared to its decrement due to the increased physical quenching (steric hindrance). The observed negative activation energies for these substrates may be interpreted as the superposition of these effects.

The decrease in ϕ and the deviation of the Stern-Volmer plot at higher concentrations of the multidentate alcohols (Figs. 3 and 8) may be partly due to the increase in the viscosity which depresses the bimolecular collision between the reactants. However, some other significant effects must be operative, since the decrease in ϕ and the deviation of the Stern-Volmer plot at higher concentrations of the multidentate alcohols are far beyond the effect of increased viscosity.

The stronger affinities of the multidentate alcohols to uranyl ions will accelerate the reverse recombination reactions of the primary redox intermediates, and the higher viscosity of these solutions will depress the secondary bimolecular process (the disproportionation processes of the primary intermediates): both lead to additional increase in the physical quenching constants.

The authors wish to thank Miss S. Yamamura for her assistance.

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[6] C. K. Jørgensen, "Inorganic Complexes," Academic Press, London, (1963), p. 101.

[7] a) A. Heller and E. Wasserman, *J. Chem. Phys.*, **42**, 949 (1965); b) G. A. Crosby, *Molecular Crystals*, **1**, 37 (1966); c) N. Filipescu and G. W. Mushrush, *J. Phys. Chem.*, **72**, 3516 (1968).

[8] a) E. Rabinowitch and R. L. Belford, "Spectroscopy and Photochemistry of Uranyl Compounds," Pergamon Press, London, (1964), pp. 91—183; b) S. Sakuraba and R. Matsushima, This Bulletin, **43**, 1950 (1970).

[9] R. Matsushima, *J. Amer. Chem. Soc.*, **94**, 6010 (1972).