at room temperature (see Figure 5) but with further irradiation the emission intensity decreases. The samples appeared to be photochemically stable at 77°K. The excitation spectrum of the long-lived emission which we purposely generated photochemically was identical with that observed in the other 1-indanone samples. Entirely similar photochemical effects are observed for I as well as 1-tetralone as the results shown in Figure 5 demonstrate. These observations with I and 1-tetralone appear to confirm the generality of this effect. The fact that Kanda, *et al.*,[5] did not observe long-lived emission from 1-tetralone might simply be due to their choice of concentrations.

We have attributed the short-lived emissions of 1-indanone, I, and 1-tetralone to emission from a $^3(n,\pi^*)$ state. Since the emission spectra which have been published before have been mixtures of short- and long-lived components, we have presented in Figure 6 emission spectra which were obtained under conditions such that the long-lived component is either absent or negligible. We have shown that the long-lived emissions are due to photoreduction products which are generated at room temperature, but we have not identified these photoproducts. Although pinacols are the major photoreduction products from 1-indanone,[13] these compounds are not phosphorescent. It is possible, however, to observe the long-lived emission from pinacol solutions if they are first irradiated for 30 sec at room temperature. The excitation spectrum of the long-lived phosphorescence (weak bands extending out to about 355 nm) indicates that emitting species still contain a carbonyl group conjugated with the aromatic ring, but beyond this we have no further information about the nature of the phosphorescent products.

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Reduction of the Mercuric Ion Induced by the Photolysis of the Uranyl–Organic Systems

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Abstract: Reduction of the mercuric ion induced by the photoredox reactions of the uranyl–organic systems has been studied both in aqueous and in 10% polyvinyl alcohol (PVA) solutions with the irradiation of $\lambda \geq 3650$ Å at room temperature. It appeared that the mercuric ion was reduced by the intermediate species formed in the primary photoredox reaction between the excited uranyl ion and ethanol. The formation of the uranium(IV) was completely inhibited by the mercuric ion, while acetaldehyde formation was not retarded. The molar ratios were $[\mathrm{U(IV)}]/[\mathrm{aldehyde}] = 0$, and $-\Delta[\mathrm{HgCl_2}]/[\mathrm{aldehyde}] = 2$, for the deoxygenated aqueous solutions. The reaction in the viscous PVA solution led to a uniform suspension of mercurous chloride, and the change in its optical density was followed with the time of irradiation. The mercuric reduction was also found in the photoredox reactions of other systems than the ethanol–uranyl system. The high photosensitivity suggested utility for a photographic process.

In the course of the study of the inhibitory effects on the photolysis of the uranyl–organic systems, the mercuric ion was found to be a highly sensitive and selective scavenger of the intermediates. When a 20% aqueous alcohol solution containing 0.005 *M* mercuric chloride and 0.01 *M* uranyl nitrate was exposed to visible light for 10 sec using a 500-W incandescent lamp, there appeared a turbidity and the transmittance of the solution fell below 10% (per 1 cm depth), which was not observed in the absence of either the uranyl ion or alcohols. The high photosensitivity was retained in the viscous polyvinyl alcohol (PVA) solution, suggesting its utility for a photographic process. Recently, the self-quenching reaction of the uranyl ions in a polymer solution has been reported,[1] while photographic properties of polymeric mercurous compound have been studied.[2]

In the present work the reduction of the mercuric ion by the intermediate species formed in the photolysis of the uranyl–organic systems was investigated and a preliminary examination on the possible application to photographic purposes was made.

Experimental Section

Doubly distilled water and guaranteed reagents were used, while polyvinyl alcohol was chemical grade (Kanto Chemicals No. 500, No. 2000). While deoxygenated aqueous solutions were used for the determination of the products (uranium(IV), aldehyde, and the disappearance of the mercuric ions), measurements of the relative rate of the mercuric ion reduction were carried out in the viscous 10% PVA solution without deoxygenation, as follows. By an addition of aqueous ethanol solution of PVA to a mixture of mercuric chloride and uranyl nitrate, aqueous solutions containing 10% PVA, 20–25% ethanol, 0.005–0.02 *M* mercuric chloride, and 0.005–0.04 *M* uranyl nitrate were prepared in the dark. The viscous solution was placed into an 1-cm depth photometer cell and exposed to light of $\lambda \geq 3650$ Å using a 100-W high-pressure mercury lamp and glass filters (UV-35, UV-39) so that only the uranyl ions absorbed the incident light, the change in the transmittance due to turbidity formation being followed at short intervals during the time of irradiation. The use of the PVA solution had the advantage, besides a practical requirement for preparation of the photosensitive plates, that in such viscous solution the turbidity was

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(1) I. A. Taha and H. Morawetz, *J. Amer. Chem. Soc.*, **93**, 829 (1971).
(2) S. Suzuki and K. Sugita, *Bull. Chem. Soc. Jap.*, **44**, 641 (1971).

retained as a (macroscopically) uniform suspension to allow direct measurement (densitometry).

Concentration of the uranium(IV) was estimated from its absorption at 650 nm, while mercuric ion concentration was determined colorimetrically using diphenylthiocarbazone.[3] Aldehydes were determined colorimetrically as their 2,4-dinitrophenylhydrazone derivatives as previously described.[4]

Results and Discussion

Reduction of Hg(II) Induced by the Photolysis of Various Systems. Table I shows the photosensitized reduction of the mercuric ion by various systems in normal (in the absence of PVA) solutions to give the fine precipitation which is assumed to be mercurous chloride.[5]

Table I. Reduction of the Mercuric Ion Induced by the Photolysis of Various Systems with λ ≥ 3650 Å

Sensitizer	Concn, M	Substrate	Concn, M (or %)	Amount of ppt
Uranyl	0.02	Ethanol	0.02	Heavy[a]
Uranyl	0.02	Lactic acid	0.2	Heavy[a]
Uranyl	0.02	Acrylonitrile	0.2	Nil
Uranyl	0.02	$K_2C_2O_4$	0.2	Heavy[a]
Benzophenone	0.02	2-Propanol	(80)	Heavy[b]
Benzophenone	0.02	2-Propanol	(100)	Heavy[c]
p-Quinone	0.02	Ethanol	0.2	Slight
p-Quinone	0.02	$K_2C_2O_4$	0.2	Slight
Biacetyl	0.04	2-Propanol	0.2	Nil
Iodine	0.02	Ethanol	(50)	Nil

[a] In the absence of organic substrates no precipitate was formed. The photoprecipitation in the absence of the uranyl ions was slow enough to be negligible compared to the rapid precipitation in the presence of the sensitizers, under these conditions. [b] No precipitate was formed either in the absence of benzophenone or in the absence of mercuric chloride. [c] 0.02 M mercuric nitrate was used, while 0.02 M mercuric chloride was used for other solutions.

It seems qualitatively that alcohol radicals are less effective for the mercuric reduction, while some other organic radicals (such as benzophenone radical and oxalic ion radical) and the uranium(V) species are effective. It may be noteworthy that the uranyl ion photosensitized free-radical polymerization[6,7] of acrylonitrile, which does not involve the uranium(V) species,[7] does not induce the mercuric reduction at all.

Stoichiometry. Table II shows the selective inhibitory effects of mercuric chloride on the photoredox reaction of the uranyl–alcohol system in deoxygenated aqueous solutions. The formation of the uranium(IV) species is completely inhibited by the mercuric ions, while aldehyde formation is not greatly affected. Since neither irradiation of the Hg(II)–U(IV) system (in the absence of the organic substrates) nor that of the Hg(II)–U(VI) system led to the reduction of the mercuric ion, the induced reduction of the mercuric ion should be due to the intermediate U(V) species[4,8] formed in the primary act between the excited uranyl ion and the organic substrates. The molar ratio, $-\Delta[HgCl_2]/[(CH_3)_2CO]$, is essentially 2 in the deoxygenated solution, in agreement with that expected from the mechanism

Table II. Reduction of the Mercuric Ion and the Molar Ratios of the Products[a]

Irradiation time, min	$[HgCl_2]$ init $\times 10^2$ M	$[CH_3CHO]$ $\times 10^3$ M	[U(IV)] $\times 10^3$ M	$-\Delta[HgCl_2]$[b] $\times 10^3$ M
10	0.00	1.47	1.45	
10	0.80	1.10	0.00	2.20
15	1.00	1.25	0.00	2.04
30	1.00	1.98	0.00	3.80
30[c]	1.00	2.52	0.00	3.60

[a] Irradiation with λ ≥ 3650 Å, in deoxygenated aqueous solution (0.04 M $HClO_4$). [b] The mercuric ion disappearance in solution. [c] In the presence of dissolved oxygen.

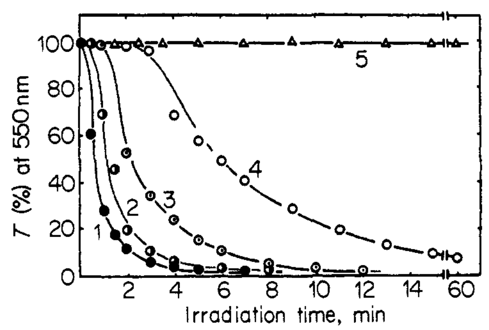

Figure 1. Dependence of the rate on the uranyl ion concentration: $[HgCl_2]$, 0.02 M; $[HClO_4]$, 0.04 M; [PVA], 10%; [ethanol], 20%; $[UO_2(NO_3)_2]$, 0.16 M (●), 0.04 M (◑), 0.02 M (◎), 0.01 M (○), 0.00 M (△); temperature, 25°; λ ≥ 3650 Å.

$$U(VI) + h\nu \longrightarrow U(VI)^* \quad (1)$$

$$U(VI)^* + R_1R_2CHOH \longrightarrow U(V) + R_1R_2\dot{C}OH + H^+ \quad (2)$$

$$U(V) + Hg(II) \longrightarrow U(VI) + Hg(I) \quad (3)$$

$$2R_1R_2\dot{C}OH \longrightarrow R_1R_2C{=}O + R_1R_2CHOH \quad (4)$$

Therefore, both oxidation of the alcohol radical by the mercuric ion, $R_1R_2\dot{C}OH + Hg(II) \rightarrow R_1R_2C{=}O + Hg(I) + H^+$, and that by the ground state uranyl ion, $R_1R_2COH + U(VI) \rightarrow R_1R_2C{=}O + U(V) + H^+$, should be excluded.

The quantum yield of mercuric reduction, ϕ_m, is therefore equal to $2\phi_A$ where ϕ_B is the quantum yield of aldehyde formation.[4]

In contrast to the unreactivity of the mercuric ion with the alcohol radical, the intermediate U(V) species is completely reduced by the mercuric ion, showing high selectivity. The high sensitivity and selectivity of the mercuric ion would be useful for the scavenging studies of the reaction intermediates in other systems.

Reaction in PVA Solution. Since the mercurous chloride formed in the highly viscous PVA solution is maintained as a uniform suspension and the optical density at arbitrary wavelength is approximately proportional to its concentration, the relative rate of the reaction is obtained by following the change in the transmittance of the solution against the irradiation time.

Figure 1 shows the relative rate of the turbidity formation with different uranyl concentration in the 10% aqueous PVA solution. The turbidity formation was neither found in the dark reaction for 3 days at room temperature nor in the photolysis in the absence

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(3) D. Polley and V. L. Miller, *Anal. Chem.*, 27, 1162 (1955).

(4) S. Sakuraba and R. Matsushima, *Bull. Chem. Soc. Jap.*, **43**, 2359 (1970).

(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 613–614.

(6) V. Mahadevan and M. Santappa, *J. Polym. Sci.*, **50**, 361 (1961).

(7) (a) K. Venkatarao and M. Santappa, *ibid., Part A-1*, **5**, 637 (1967); (b) K. Venkatarao and M. Santappa, *ibid., Part A-1*, **8**, 3429 (1970).

(8) (a) L. J. Heidt, *J. Amer. Chem. Soc.*, **76**, 5962 (1954); (b) S. Sakuraba and R. Matsushima, *Bull. Chem. Soc. Jap.*, **43**, 1950 (1970); **44**, 1278 (1971).

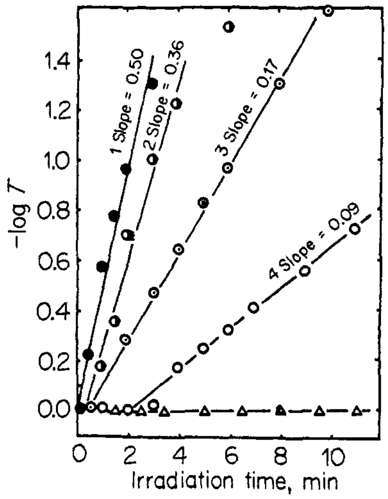

Figure 2. The alternative plot of Figure 1: [$UO_2(NO_3)_2$], 0.16 *M* (●), 0.04 *M* (◐), 0.02 *M* (⊙), 0.01 *M* (○), 0.00 *M* (△).

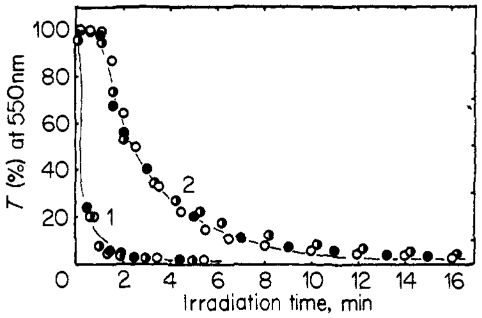

Figure 3. Dependence of the rate on the mercuric ion concentration: [$UO_2(NO_3)_2$], 0.04 *M*; [$HClO_4$], 0.04 *M*; [PVA], 10%; [ethanol], 20%; [$HgCl_2$], 0.005 *M* (○), 0.04 *M* (◐), 0.08 *M* (●); temperature, 25°; $\lambda \geq 3650$ Å; curve 1, exposed at 4-cm distance, curve 2, at 12-cm distance.

of the uranyl ion (plot 5 in Figure 1). Figure 1 shows that the relative rate is increased with the increase in the uranyl concentration, and the alternative plot (Figure 2) shows that there exists an approximately linear relationship between the optical density and the irradiation time in the initial stages of the reaction.

The relative rate is proportional to the uranyl concentration up to 0.04 *M*, *i.e.*, to the number of light quanta absorbed, since the absorbance of the solution in the visible region is small. This proportionality is consistent with the mechanism proposed.

The effects of concentration of mercuric chloride and acid on the rate seem to be less important as shown in Figures 3 and 4, indicating that the rate-determining step is the α-hydrogen abstraction from the alcohol molecule by the excited uranyl ion.

Other Sensitizers. The mercuric reduction induced by the photodecomposition of oxalato complexes[9] (or oxalic acid) which are well known to be photosensitive was tested in the PVA solution as well (Figure 5).

It should be noticed that the photosensitizing efficiencies of the transition metal ions toward the mercuric reduction are considerably decreased by complexing with the oxalate ions, while the oxalate ion in the absence of the metal ions seems to be effective (curve 6) in spite of its low absorbance in the visible region.

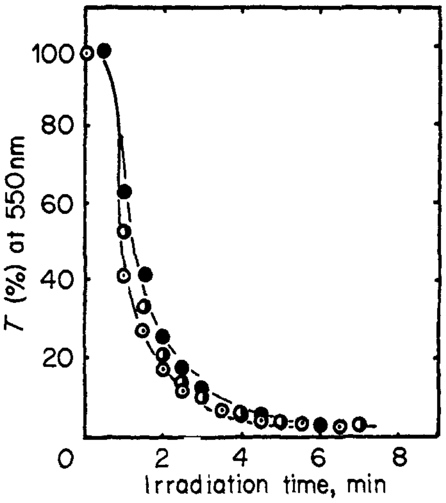

Figure 4. Effect of acids on the rate: ●, 0.04 *M* $HClO_4$; ◐, 0.04 *M* CH_3CO_2H; ⊙, no addition of acid; other conditions were the same as those in Figure 1.

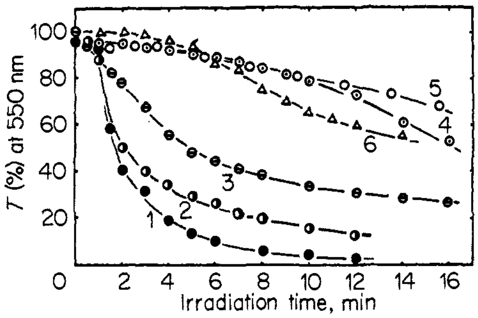

Figure 5. Comparison of the rate with those of some other systems in 10% aqueous PVA solution (25°, $\lambda \geq 3650$ Å): 1, 0.04 *M* $UO_2(NO_3)_2$ and 20% ethanol; 2, 0.04 *M* $UO_2(NO_3)_2$ and neither ethanol nor oxalate ion is added; 3, 0.04 *M* $UO_2(NO_3)_2$ and 0.04 *M* $K_2C_2O_4$; 4, 0.04 *M* $Fe(NO_3)_3$ and 0.04 *M* $K_2C_2O_4$; 5, 0.02 *M* $MnSO_4$ and 0.04 *M* $K_2C_2O_4$; 6, 0.04 *M* $K_2C_2O_4$. Each solution contains 0.22 *M* $HClO_4$, 0.02 *M* $HgCl_2$, and 10% PVA, besides the above sensitizers.

The uranyl–oxalate system (curve 3) is less effective even than one containing neither oxalate ion nor ethanol (curve 2). Further, both the ferric oxalate and the manganese oxalate systems are not more effective than that containing neither metal ion (curves 4 and 5). These results suggest that not all the decomposition intermediates[10] of oxalate such as radical ions are effective toward the mercuric reduction or the intermediate species which are effective toward the mercuric reduction are rapidly oxidized by the transition metal ions prior to the oxidation by the mercuric ion. Considerable turbidity forms even in the absence of ethanol, though slightly less than in its presence (curve 1), indicating the oxidation of polyvinyl alcohol by the excited uranyl ion. The reaction occurred much more

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(9) (a) C. A. Parker, *Trans. Faraday Soc.*, **50**, 1213 (1954); (b) T. B. Copestake and N. Uri, *Proc. Roy. Soc., Ser. A*, **228**, 252 (1955); (c) S. Sakuraba and S. Ikeya, *Bull. Chem. Soc. Jap.*, **30**, 662 (1957); (d) A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, **80**, 3865 (1958); (e) G. B. Porter, J. G. W. Doering, and S. Karanka, *ibid.*, **84**, 4027 (1962); (f) D. H. Volman and J. R. Seed, *ibid.*, **86**, 5095 (1964).

(10) (a) C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, **63**, 22 (1959); (b) W. W. Wendlandt and E. L. Simmons, *J. Inorg. Nucl. Chem.*, **27**, 2317 (1965); (c) D. R. Eaton and S. R. Suart, *J. Phys. Chem.*, **72**, 400 (1968); (d) L. J. Heidt, G. W. Tregay, and F. A. Middleton, *ibid.*, **74**, 1876 (1970).

rapidly when a 500-W incandescent lamp without filters was employed as a light source. It is believed that the process using fined application in photography will be useful and further examination along this line (including the preparation of the photosensitive plates) is in progress.

Structure of Transition States in Organic Reactions. General Theory and an Application to the Cyclobutene–Butadiene Isomerization Using a Semiempirical Molecular Orbital Method

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Abstract: A method for locating and identifying transition states for systems with many degrees of freedom is described. The principle feature of the method is the location of saddle points on the potential energy surface by the employment of a generalized least-squares technique to minimize the Euclidian norm of the gradient of the potential energy function. For semiempirical molecular orbital methods the technique is relatively economical to use, thus permitting a variety of organic reactions to be studied. As an example, the transition state for the cyclobutene–butadiene isomerization is calculated using the MINDO/2 molecular orbital method. The results of this study are somewhat unexpected.

A detailed understanding of the dynamics and stereochemistry of organic reactions requires, above all, a knowledge of the many-dimensional potential energy surface. The very dimensionality of this surface, however, precludes its evaluation for all but the simplest systems. The theoretical study of a reaction involving only four atoms, for example, would require a million evaluations of the potential energy function if only ten grid points for each degree of freedom are chosen. To reduce this problem to one of a tractable size, two general approaches have been employed. The first type of approach seeks to reduce the dimensionality of the surface by eliminating certain degrees of freedom. In many cases, for example, the length of carbon–hydrogen bonds can be assumed to remain relatively unchanged throughout the course of the reaction. Thus, the degrees of freedom corresponding to these C–H bond lengths can be eliminated from consideration. However, for most organic reactions, it is unlikely that the dimensionality can be sufficiently reduced to a manageable number of degrees of freedom without placing unrealistically severe constraints on the system. A related technique involves choosing one or two degrees of freedom as independent variables of the potential energy and to allow the system to relax by optimizing the remaining degrees of freedom for each value of the independent variables. This type of approach, however, is computationally expensive, and the resulting surface may very well fail to include the transition state. The second type of general approach involves consideration of all the degrees of freedom of the system but seeks only to locate certain chemically interesting points on the potential energy surface. For a one-step reaction, these points would be the local minima corresponding to the equilibrium geometries of reactants and products and a col or saddle point which separates these local minima. The lowest energy saddle point lying between two such local minima corresponds to the transition state or activated complex for the reaction. The calculation of equilibrium geometries is a relatively straightforward process. It involves only the minimization of the potential energy function with respect to the degrees of freedom of the molecule. Geometries of even moderately large organic molecules can be calculated relatively economically when semiempirical molecular orbital methods are used.[1] Certain types of transition states can also be located using energy-minimization techniques. In reactions for which the reactants and products are identical in structure, intermediate configurations can generally be found which are of a different symmetry. Minimizing the energy within this symmetry will lead to a stationary point which may be a transition state for the reaction. Well-known examples of this are the internal rotations of ethane and ethylene about the C–C bonds and the umbrella inversion of ammonia. Another example is that of the Cope rearrangement, which has been recently studied by Dewar and coworkers.[2] In the general case, however, transition states cannot be determined by minimizing the energy within a given symmetry so that alternative methods of seeking these points must be devised.

The purpose of this article is to describe a valid computational method of locating transition states on the potential energy surface and to apply the method to a simple organic reaction: the isomerization of cyclobutene to butadiene. The semiempirical MINDO/2 molecular orbital method[3] was used for this particular

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[1] J. W. McIver, Jr., and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971).

[2] A. Brown, M. J. S. Dewar, and W. W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970).

[3] (a) M. J. S. Dewar and E. Haselbach, *ibid.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).