Photoreactions of the Uranyl Ion with Arylaldehydes in Solution

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Irradiation of benzaldehyde in a deoxygenated aqueous acetone solution in the presence of the uranyl ion with light of $\lambda \geqq 365$ nm gives the U(IV) species and benzil (**1**) as the main photoredox products, and small amounts of 4-hydroxy-4-phenylbutan-2-one (**2**), *trans*-4-phenyl-3-buten-2-one (**3**), and an unidentified product (**4**). None of them are formed in the absence of the uranyl ion. The products **2** and **3** are assumed to be formed by the uranyl ion-photocatalyzed condensation of benzaldehyde with acetone. Irradiation of acetophenone in the presence of the uranyl ion gives no photoproducts, though the uranyl emission is effectively quenched. *p*-Methoxybenzaldehyde and *p*-chlorobenzaldehyde give the corresponding 4,4′-disubstituted benzils respectively by irradiation under similar conditions. The quantum yield for the formation of the U(IV) species decreases whereas the quenching constant increases with the increase in the electron donating power of the substituent. The physical quenching process appears to compete significantly with the chemical (redox) process. The relative importance of the physical quenching to the chemical quenching process has been estimated. As to the photocatalyzed aldol condensation, the excess vibrational energy, which the quencher and/or the quenchee would possess during or immediately after the quenching interactions, may possibly be converted into the energy of the chemical reaction.

Primary interactions of the excited uranyl ion with organic compounds in solutions may be classified into three types: a) electronic energy transfer,[1,2] b) chemical (redox) interactions such as the abstraction of active hydrogen atoms,[3-5] and c) physical quenching *via* formation and decay of excited state π-complexes[6] (with aromatic molecules). In the previous paper the formation of biacetyl by the photooxidation of acetaldehyde with the uranyl ion has been reported,[5] where the only important interactions is the chemical one.

Arylaldehydes have both physical (π-electron cloud) and chemical (aldehyde hydrogen) quenching centers in one molecule. The present paper is concerned with the photochemistry of the uranyl ion with arylaldehydes, where it may be questioned whether physical and chemical interactions are simply competitive or whether they can be interconverted to some extent.

Experimental

Materials. Benzaldehyde (guaranteed grade) was freshly distilled under reduced nitrogen pressure before use. Other chemicals were of guaranteed reagent grade and were used without further purification. Water was distilled after passing through ion exchange resins.

Quenching Constants. The relative intensities of the uranyl emission near the 510 nm peak were measured with the 436 nm excitation in 60 vol% aqueous acetone solutions containing 0.02 M uranyl nitrate, 0.1 M perchloric acid, and various concentrations of the quenchers, at 25±2 °C. Since the quenching constants were not significantly influenced by the dissolved oxygen, they were measured without deoxygenation. The measurements were carried out by means of a Hitachi 204-type fluorescence spectrophotometer.

Photolysis. 60 vol% aqueous acetone solutions of 0.2 M benzaldehydes in the presence of 0.02 M uranyl nitrate (hexahydrate) and 0.1 M perchloric acid were deoxygenated with oxygen-free nitrogen current, and were sealed in identical 7 ml ampoules. They were irradiated with light of $\lambda \geqq 365$ nm from a 100 or 400 W high pressure mercury lamp. For the quantitative experiments, a merry-go-round irradiation apparatus in a thermostat (10±1 °C) or an optical train with a suitable arrangement for obtaining a parallel light beam perpendicular to the plane of the windows of the photoreaction cells was used. Actinometry was carried out with the ferric oxalate actinometer solution. No correction was made of the quantum yields for formation of the products, though under these conditions some errors might be involved due to the inner filter effects by benzaldehyde or products and the quenching of the excited state uranyl ion by the products.

Analysis of the Photoproducts. After the elimination of acetone from the photolyzed mixture solution, the residual aqueous solution was extracted with chloroform. The chloroform layer was washed with aqueous sodium bisulfate solution to eliminate benzoic acid. The chloroform layer was, after drying and condensation, separated on PLC (silica gel 60 PF-254, Merck) into four portions (**1**, **2**, **3**, and **4**). **2**: IR, 1700 (s), 3400 (broad) cm^{-1}; NMR, δ 2.0 (s, 3H), 2.6 (d, 2H), 4.0 (s, 1H), 5.0 (dd, 1H), 7.2 (m, 5H). **4**: mp, 120.5—122 °C; IR, 1690 cm^{-1}, no OH; NMR, δ 7.1 (s, 1H), 7.5—8.4 (m, 13H). Found: C, 80.32; H, 5.45%. Calcd for $C_{14}H_{10}O_2$: C, 80.00; H, 4.76%.

The amounts of the organic products were determined by densitometry on TLC after conversion into the corresponding 2,4-dinitrophenylhydrazone derivatives. The densitometer was an OZUMOR-82 (Meika KK). The measurements of NMR and IR spectra were carried out by means of a high resolution NMR spectrometer (Hitachi R-24) and an IR spectrometer (Japan Spectroscopic IR-S).

Results and Discussion

Formation of Organic Products. From the photolysis of benzaldehyde–uranyl solution, the products **1** and **3** have been identified respectively as benzil and *trans*-4-

TABLE 1. APPROXIMATE QUANTUM YIELDS OF THE PRODUCTS FROM THE PHOTOLYSIS OF BENZALDEHYDE WITH THE URANYL ION[a)]

Product	Quantum yield
U(IV)	0.14
1	0.12
2	0.01
3	0.02
4	<0.01

a) Benzaldehyde: 0.2 M; uranyl ion: 0.02 M; perchloric acid: 0.1 M; in 60 vol % aqueous acetone at 10 °C, $\lambda \geqq 365$ nm.

phenyl-3-buten-2-one by comparing their IR and NMR spectra with those of authentic samples, while the product **2** has been assigned to 4-hydroxy-4-phenylbutan-2-one on the basis of its IR and NMR spectra. The structure of the product **4** has not been clarified, though it may be tentatively assumed to be 2-phenyl-2,3-dihydrobenzofuran-3-one. The approximate quantum yields for the products from the photolysis of uranyl-benzaldehyde solution are listed in Table 1. Benzil (**1**), which was not formed by thermal reaction at 50 °C, is the main organic product, while the products **2**, **3**, and **4** are minor ones. In the absence of the uranyl ion, however, none of them was formed by the photolysis of benzaldehyde under similar conditions. Benzoic acid which is produced by thermal autooxidation of benzaldehyde on oxposure to the air, was unlikely to be an important product of the photoreactions under the present experimental conditions.

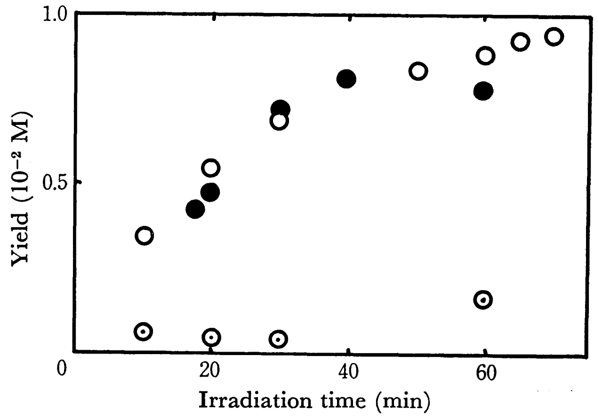

Fig. 1. Product yields at various extents of the photoreaction of benzaldehyde with the uranyl ion. Conditions are similar to those in Table 1. ○: U(IV) species, ●: product **1**, ⊙: product **2**.

Figure 1 shows that the molar ratio of the product **1** to the U(IV) species is close to unity, regardless of the extent of the photoreaction; thus **1** is the main oxidation product and it probably does not undergo any subsequent reactions. *p*-Methoxybenzaldehyde and *p*-chlorobenzaldehyde also gave the corresponding 4,4′-disubstituted benzils as the main organic products by irradiation in the presence of the uranyl ion under similar conditions. The reaction scheme for the formation of the product **1** (and also 4,4′-disubstituted benzils) may be assumed as follows, in analogy to that for the formation of biacetyl by the photooxidation of acetaldehyde with the uranyl ion:[5]

$$^{*}UO_2^{2+} + ArCH{=}O \longrightarrow UO_2^{+} + H^{+} + Ar\dot{C}{=}O$$

$$2Ar\dot{C}{=}O \longrightarrow ArCOCOAr$$

$$2UO_2^{+} \xrightarrow{H^{+}} UO_2^{2+} + \text{U(IV) species}$$

Unlike the product **1** which is the photoredox product, the products **2** and **3** are formally not the redox products but are aldol condensation products of benzaldehyde with acetone, catalyzed by the excited state uranyl ion. As to the catalyzed aldol condensation by transition metal ions in the ground states, Iwata and Emoto have recently reported the cupric ion-catalyzed condensation of aromatic aldehydes with acetone.[7] Thermal reaction of the uranyl–benzaldehyde mixture for 30 hours at 50 °C also gave the products **2** and **3**, but their amounts were much less compared to those obtained by irradiation of an identical solution for 2 hours at 10 °C with a 100 W high pressure mercury lamp. Direct irradiation (*i.e.*, in the absence of the uranyl ion) with light of 254 nm (from a 160 W low pressure mercury lamp) for 9 hours at 10 °C gave no such condensation products. These facts suggest a photocatalytic action of the uranyl ion, *i.e.*, the condensation of benzaldehyde with acetone is much more accelerated by the excited uranyl ion than by the ground state uranyl ion. In the sense that the uranyl ion is not reduced, the process is a photocatalytic one.

$$ArCH{=}O + CH_3COCH_3 \xrightarrow{^{*}UO_2^{2+}} ArCH(OH)CH_2COCH_3$$

The product **3** is assumed to be formed from the product **2** by dehydration during the analytical procedures, since **2** is easily converted into **3** by similar treatments. Hence the relative yield of the product **2** to **3** is changeable. In order to clarify the possible route for the formation of the product **4**, an investigation was made on the solution conditions of the photoreaction to give **4** (Table 2). The results show that the product **1** is unlikely to be the source of **4**, but that **4** is probably formed only by the photoreaction of benzaldehyde with the uranyl ion. The structure of **4** is, however, uncertain as yet.

TABLE 2. CONDITIONS OF THE PHOTOREACTION TO GIVE THE PRODUCT **4**

Initially added concentrations[a)]			Formation of **4**
Uranyl ion, M	Benzaldehyde, M	Benzil, M	
0.00	0.10	0.02	no
0.02	0.00	0.10	no
0.02	0.10	0.00	yes

a) Other conditions were similar to those in Table 1.

Stability of the U(IV) Species. The stabilities of the U(IV) species in solutions exposed to the air were preliminarily examined. Figure 2 shows that the stability of the U(IV) species is significantly solvent-dependent. The stability was higher at low temperature. The amount of the U(IV) species formed was determined either by rapid colorimetric analysis with arsenazo-III[8] immediately after breaking the ampoules or by the direct measurements of the absorbance at its 650 nm peak in the ampoules without exposure to the air.

Formation Quantum Yield of the U(IV) Species. Irradiation with $\lambda \geqq 365$ nm of a deoxygenated 60 vol% aqueous acetone solution of 0.2 M benzaldehyde in the presence of 0.02 M uranyl ion and 0.1 M perchloric acid leads to the reduction of the uranyl ion to give the U(IV) species which is easily identified by its characteristic absorption spectrum (430—700 nm). A series of the substituted benzaldehydes also lead to the formation of the U(IV) species upon irradiation under similar conditions. The formation quantum yields of the

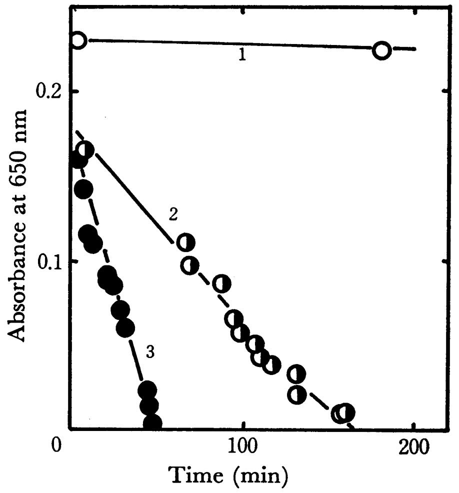

Fig. 2. Stabilities of the U(IV) species in solutions under the air. U(IV) species: 0.02 M, perchloric acid: 0.1 M; (1): in aqueous solution, (2): in 60 vol % aqueous acetone solution, (3): in 60 vol % aqueous acetone solutionin the presence of 0.2 M benzaldehyde.

TABLE 3. QUENCHING CONSTANTS (K) AND THE QUANTUM YIELDS (ϕ) OF THE U(IV) FORMATION FOR SUBSTITUTED BENZALDEHYDES

Substituent	$K\times 10^{-2}$, M^{-1}	ϕ	$\sigma^{+\mathrm{a)}}$
p-$\mathrm{N(CH_3)_2}$	93		-1.7
p-$\mathrm{OCH_3}$	17	0.06	-0.778
p-$\mathrm{CH_3}$	8.0	0.13	-0.311
H	5.0	0.16	0.000
p-Cl	4.0	0.23	0.114
m-Cl	3.3	0.25	0.391
p-$\mathrm{NO_2}$	2.0	$0.6^{\mathrm{b)}}$	0.790

a) Polar substituent constants. b) Because of the low solubility, the initial concentration of p-nitrobenzaldehyde was 0.017 M.

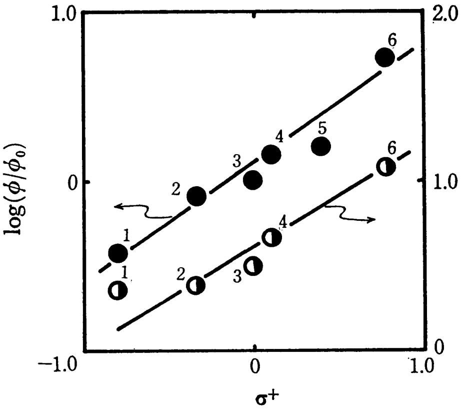

Fig. 3. Plots of $\log(\phi/\phi_0)$ and Δ vs. σ^+. Δ is the difference in the ordinates for benzaldehydes (b) and acetophenones (a) in Fig. 4. The numbering is the same as that in Fig. 4.

U(IV) are listed in Table 3. A plot of log (ϕ/ϕ_0) vs σ^+ is shown in Fig. 3, where ϕ and ϕ_0 are the formation quantum yields of the U(IV) species for the substituted and parent benzaldehydes respectively.

Unlike the systems of the uranyl–benzaldehydes, neither significant formation of the U(IV) species nor formation of organic photoproducts were detected upon irradiation of the uranyl–acetophenone system under conditions similar to those of the uranyl–benzaldehyde system.

Physical and Chemical Quenching. Quenching constants (K) of substituted benzaldehydes, obtained from the Stern-Volmer plots for the quenching of the uranyl emission in 60% aqueous acetone (containing 0.1 M perchloric acid), are listed in Table 3. The Stern-Volmer plots, $I^{\circ}/I=1+K[\mathrm{ArCH{=}O}]$, did not always give straight lines; sometimes the lines were concave downward at high concentrations of the quenchers. The quenching constants were obtained at low concentrations of the quenchers (usually, $[\mathrm{ArCH{=}O}]\leq 2\times 10^{-3}$ M).

It may be noted that the photoredox quantum yield inversely proportional to the quenching constant, which indicates that the physical and the chemical quenching processes are competing. The plot of log (K/K_0) vs σ^+ shows a straight line with a slope of $\rho=-0.7$ (where K_0 is the quenching constant of benzaldehyde), while similar plot for substituted acetophenones gives a straight line with a slope of $\rho=-1.0$ (Fig. 4). The difference in the slope of the two lines may be noted.

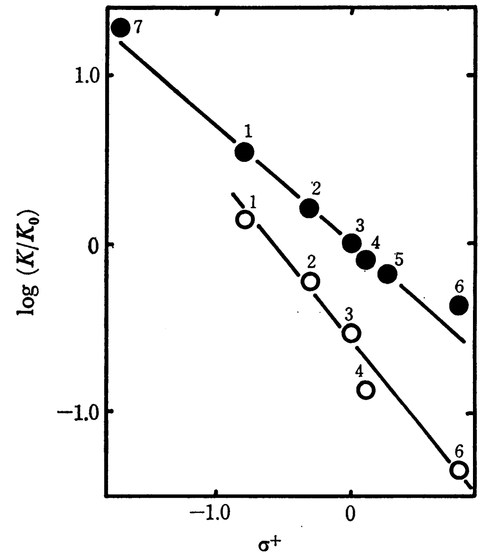

Fig. 4. Plots of $\log(K/K_0)$ vs. σ^+ for substituted benzaldehydes (●) and acetophenones (○). The substituents are, 1: p-methoxy, 2: p-methyl, 3: nonsubstituted, 4: p-chloro, 5: m-chloro, 6: p-nitro, and 7: p-dimethylamino, groups.

An electronic excitation energy transfer from the uranyl ion to these substrates will not occur, since it is a highly endothermic process. Quenching of the uranyl emission by acetophenone may be assumed to be essentially a physical quenching process, since it occurs without final chemical changes, while quenching by benzaldehydes involves both chemical and physical processes. From this point of view, the difference in the slope of the two lines in Fig. 4 may be assumed to reflect the chemical quenching of benzaldehydes. Thus the difference in the ordinate of the two plots in Fig. 4, $\Delta = \log (K/K_0)_b - \log (K/K_0)_a$, which is assumed to be a measure of the chemical part of the quenching interactions, is plotted against σ^+ (open circles in Fig. 3). Here, a and b refer to the series of acetophenones and benzaldehydes, respectively. Figure 3 shows that Δ and $\log (\phi/\phi_0)$ are roughly parallel and suggests that the rate-determining steps are similar (abstration of the aldehyde hydrogen atoms). The apparent positive slope (ρ) in Fig. 3 may indicate that the chemical process is depressed by the competitive physical quenching process as the efficiency of the latter process is increased with the decrease in σ^+.

On the assumption of a simple scheme for the quenching of the uranyl emission by benzaldehydes, an approximate estimation of the relative importance of the physical and chemical (redox) quenching processes may be available. The main scheme may be drawn as follows for the photoredox reaction:

$$^*UO_2^{2+} + ArCH{=}O \underset{k_d}{\overset{k_e}{\rightleftharpoons}} {}^*UO_2^{2+} \cdots ArCH{=}O$$

$$\xrightarrow{k_p} UO_2^{2+} + ArCH{=}O + \text{heat} \qquad (1)$$

$$\xrightarrow[k_r]{} UO_2^{+} + Ar\dot{C}{=}O + H^+ \qquad (2)$$

$$2UO_2^{+} \xrightarrow[\text{rapid}]{H^+} UO_2^{2+} + U(IV)\text{ species} \qquad (3)$$

$$2Ar\dot{C}{=}O \xrightarrow[\text{rapid}]{} ArCOCOAr \qquad (4)$$

Since the molar ratio of the redox products (benzils and the U(IV) species) is near unity, the following processes are assumed to be less important:

$$Ar\dot{C}{=}O + U(IV) \xrightarrow{H^+} UO_2^{+} + ArCH{=}O$$

$$UO_2^{+} + ArCH{=}O \longrightarrow U(IV) + Ar\dot{C}{=}O + H^+$$

The steady state approximation to $^*UO_2^{2+}$, $^*UO_2^{2+}\cdots ArCH{=}O$, $Ar\dot{C}{=}O$ and UO_2^+ may eventually yield

$$\frac{1}{\phi} = \left(2 + \frac{2k_p}{k_r}\right) + \frac{2(k_d + k_p + k_r)}{\tau_0 k_e k_r [ArCH{=}O]} \qquad (5)$$

Here, τ_0 is the emission lifetime of the excited uranyl ion in the absence of benzaldehydes. Equation 5 indicates that the plots of ϕ^{-1} *vs* [benzaldehyde]$^{-1}$ should give a straight line with an intercept not smaller than 2. Figure 5 agrees with Eq. 5. From Eq. 5 the ratio of the physical and the chemical (redox) quenching rate constants, k_p/k_r, is given by $k_p/k_r = (\text{intercept} - 2)/2$. The values obtained from Fig. 5 are listed in Table 4.

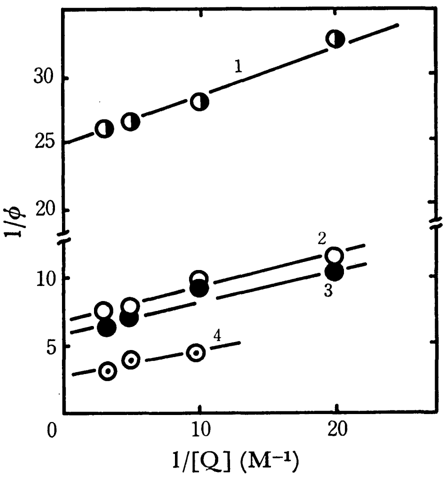

Fig. 5. Plots of $1/\phi$ *vs.* 1/[ArCH=O], for *p*-methoxy (1), *p*-methyl (2), nonsubstituted (3), and *p*-chloro (4), benzaldehydes. Conditions are similar to those in Table 1.

Table 4. Rate parameters for the photooxidation of substituted benzaldehydes with the uranyl ion

Substituent	I_s[a]	k_p/k_r[b]
p-OCH$_3$	25	11.5
p-CH$_3$	6.8	2.4
H	6.0	2.0
p-Cl	2.5	0.25

a) Intercept of the plot in Fig. 5. b) $k_p/k_r = (I_s - 2)/2$.

These results shows that significant physical quenching is competing with the chemical (redox) quenching process, or that the excess vibrational energy (which the quencher and/or the quenchee would possess during or immediately after the physical quenching interactions) is unlikely to be effective for causing the redox reaction. On the other hand, the uranyl ion-photocatalyzed aldol condensation can be assumed to involve the conversion of the excess vibrational energy to that for the chemical process.

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