On the Photoreduction of Benzophenone in Isopropyl Alcohol

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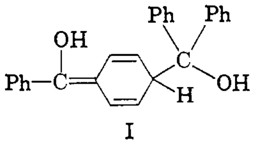
Abstract: 1-(Phenylhydroxymethylene)-4-(dimethylhydroxymethyl)-2,5-cyclohexadiene is proposed to be the stable intermediate (In) in the photoreduction of benzophenone in pure isopropyl alcohol. The phosphorescence and phosphorescence excitation spectra of In were obtained by matrix isolation in frozen isopropyl alcohol at 77°K. The absorption spectrum of In determined by the use of actinometry and verified by the excitation spectrum was used to follow the kinetics of the dark reaction following irradiation. The proposed mechanism is consistent with all observed data and explains the erratic quantum yield results reported previously.

The nature of the intermediate in the photoreduction of benzophenone (Ph_2CO) in isopropyl alcohol in the absence of air has remained a controversial subject for roughly 10 years. Different adducts between diphenylhydroxymethyl ($Ph_2\dot{C}OH$) or dimethylhydroxymethyl ($Me_2\dot{C}OH$) free radicals and benzophenone (Ph_2CO) were first suggested.[1-4] Later, charge-transfer complexes between free radicals $Me_2\dot{C}OH$ and $Ph_2\dot{C}OH$ or between $Me_2\dot{C}OH$ and the $Me_2\dot{C}OH$–Ph_2CO adduct were proposed by Bäckström, *et al.*[5] However, absence of esr signals has eliminated a free-radical formulation for the long-lived colored intermediate.[6-8] More recently Schenck, *et al.*,[9,10] interpreted a number of experimental observations by assuming the intermediate to be a simple adduct of two $Ph_2\dot{C}OH$ radicals, "isobenzopinacol" (I or II).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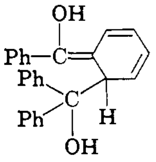
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Unlike the photoreduction of Ph_2CO in benzene in the presence of benzhydrol,[11-13] the quantum yield in 100% isopropyl alcohol varied erratically,[1,8,13] depending on concentration of Ph_2CO, irradiation time, and interval allowed before admission of air. These facts, together with the observed properties of the intermediate, namely, its stability, reducing capability, indicator behavior, diamagnetism, and rate of reaction with O_2, were difficult to explain simultaneously.

In the present work we have obtained the absorption spectrum of the intermediate by three paths: actinometry, low-temperature phosphorescence excitation in a rigid matrix, and many-component absorption spectroscopy. In addition, the kinetics of the "dark reaction" was followed and used to verify the proposed reaction mechanism, which is consistent with all observed data and explains previous "erratic" results.

Experimental Section

Reagent grade benzophenone (Fisher) was recrystallized repeatedly from cyclohexane and dissolved in Spectrograde isopropyl alcohol (Fisher). Solutions of 10^{-3}–10^{-4} *M* were degassed by several cycles of freeze–pump–thaw, either in Thunberg cells or in sealable 1-cm absorption cells provided with outgassing reservoirs. Absorption spectra were recorded on the Cary Model 14 spectrophotometer in double-beam mode.

The irradiations were carried out with light from a water-cooled 1000-W AH-6 mercury lamp except for actinometric measurements, in which a Bausch and Lomb high-intensity monochromator, Model 5, with high-pressure mercury source was used. The ferrioxalate actinometer of Hatchard and Parker[14] was employed to monitor light intensities. After irradiation, the sealed cell was kept in the dark and the changes in the absorption spectrum were measured at intervals throughout the dark reaction until the absorption remained unchanged. We noticed that over the long time required for the completion of the dark reaction (days), some air diffused inside the cells provided with ground-glass greased joints. Therefore, the results reported herein are those obtained in flame-sealed cells with degassing side reservoirs.

For the matrix-isolation experiments the benzophenone solutions were degassed in sealable quartz tubes and frozen in liquid nitrogen in the coldfinger dewar of the Aminco-Bowman spectrophotofluorimeter. The quality of the pure isopropyl alcohol glass improved significantly upon degassing. Both emission and excitation spectra were determined in samples that were irradiated at room temperature and subsequently frozen at 77°K.

Results and Discussion

Isosbestic Points. Changes in the absorption spectrum after successive irradiations of 10^{-3} and 10^{-4} *M* Ph_2CO in degassed absolute isopropyl alcohol verified the existence of two isosbestic points at 288 and 227 mμ, first observed by Schenck, *et al.*[9] The solutions remained "isosbestic" for periods longer than 0.5 hr after the initial radiation, but, if the dark reaction was allowed to proceed longer or if the irradiation was excessive, the absorption spectrum no longer passed through the two points. The presence of the isosbestic points clearly establishes the existence of only two absorbing components, Ph_2CO and In, throughout our irradiation times, which never exceeded 15 min.

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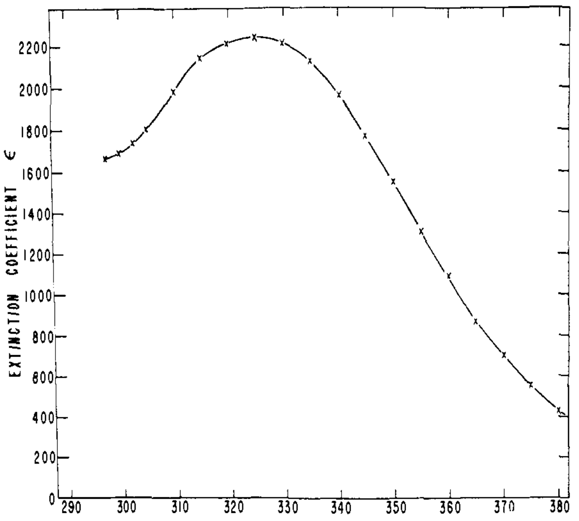


Figure 1. Absorption spectrum of intermediate, In, calculated from multicomponent spectroscopy and verified actinometrically.

Absorption Spectrum of Intermediate (In). (a) Actinometry. Since immediately after irradiation only Ph_2CO and In are present and since one In molecule appears from one Ph_2CO, actinometric determination of the number of quanta absorbed by Ph_2CO gave directly the concentration of In (the quantum yield for the photochemical conversion $Ph_2CO \rightarrow$ In was taken to be unity[1,13]); we assume that whatever excitation energy is absorbed by In during irradiation is subsequently passed on to Ph_2CO by triplet–triplet collisional transfer. The energetic location of the two triplets and a very efficient intersystem crossing in In seem to favor this process (see below). The absorption spectrum of In, easily derived from the absorption of the mixture of known In and Ph_2CO concentration, is displayed in Figure 1.

(b) Low-Temperature Trapping. Figure 2 shows the emission and excitation spectra of In in frozen isopropyl alcohol glass at liquid N_2 temperature. Both spectra were corrected for the spectral output of the Xe lamp and 1P28 photomultiplier response.[15,16] The corrected excitation spectrum closely resembles the calculated absorption spectrum in Figure 1.

Because the intense blue phosphorescence emission of In, which displays no vibrational structure, overlaps extensively the $T \rightarrow S_0$ emission of Ph_2CO,[17,18] the energy-transfer process ${}^3In + Ph_2CO \rightarrow In + {}^3Ph_2CO$ is operable.

After thawing the glass and admitting air, samples which had contained almost exclusively In displayed upon refreezing the original characteristic Ph_2CO emission. This is the first direct confirmation that Ph_2CO is regenerated from In reacting with atmospheric O_2. The reaction, however, is slow, on the order of hours, and extended exposure to air is required to remove completely the In emission. The long-lived (τ = 8 sec) phosphorescence of benzopinacol was absent immediately following irradiation, even for high $Ph_2CO \rightarrow$ In conversions. The emission spectrum of the pinacol was separately determined from pure samples in the same isopropyl alcohol rigid matrix. It displayed only long-lived phosphorescence in a broad band centered at 380 mμ with shoulders at 360, 375, 390, and 460 mμ.

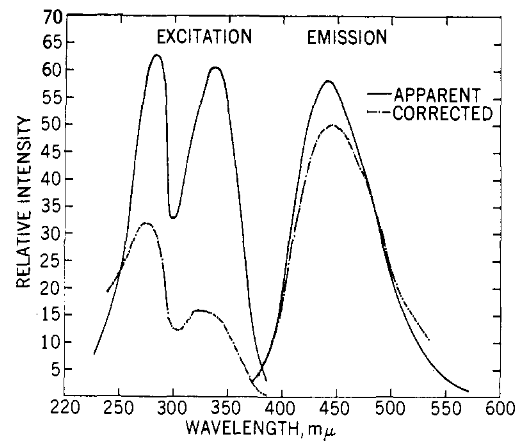


Figure 2. Phosphorescence and phosphorescence excitation spectra of intermediate, In, in isopropyl alcohol glass at 77°K.

(c) Multicomponent Absorption Spectroscopy. For low conversions only Ph_2CO and In are present at the end of the irradiation and only Ph_2CO, benzopinacol, and acetone are present at the end of the dark reaction. Assuming that two Ph_2CO molecules disappear finally for each photon absorbed (see Mechanism), one can calculate the absorption spectrum of In with the following expression

$$\epsilon_{In} = \epsilon_{Ph_2CO} - (2\epsilon_{Ph_2CO} - \epsilon_{Me_2CO} - \epsilon_{pinacol}) \times (a^{t_1} - a^{t_0})/(a^{t_\infty} - a^{t_0})$$

where ε's are extinction coefficients at wavelength λ and a's are the absorbancies before irradiation (t_0), after irradiation (t_1), and at the end of the dark reaction (t_∞) at the same λ. For $Ph_2CO \rightarrow$ In conversions in excess of 50%, the products at the end of the dark reaction are benzopinacol, acetone, and intermediate. In such runs, the absorption spectrum of In is calculated from the second-degree equation

$$c_0\epsilon_{In}^2 - [c_0(\epsilon_{pinacol} + \epsilon_{Me_2CO}) - a^{t_0} - a^{t_\infty} + 2a^{t_1}]\epsilon_{In} - a^{t_\infty}\epsilon_{Ph_2CO} + a^{t_1}(\epsilon_{pinacol} + \epsilon_{Me_2CO}) = 0$$

where c_0 is the concentration of benzophenone at time t_0. Figure 1 shows the calculated spectrum of In from a typical run of 73% $Ph_2CO \rightarrow$ In conversion.

Mechanism. The reaction can be represented by steps 1–5 below, in agreement with all observed data,

$$Ph_2CO \xrightarrow{h\nu} {}^1Ph_2CO \longrightarrow {}^3Ph_2CO \tag{1}$$

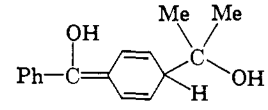
$${}^3Ph_2CO + Me_2CHOH \longrightarrow Ph_2\dot{C}OH + Me_2\dot{C}OH \tag{2}$$

$$Ph_2\dot{C}OH + Me_2\dot{C}OH \longrightarrow In \tag{3}$$

$$In + Ph_2CO \xrightarrow{k_D} 2Ph_2\dot{C}OH + Me_2CO \tag{4}$$

$$2Ph_2\dot{C}OH \longrightarrow Ph_2C(OH)C(OH)Ph_2 \tag{5}$$

where In is structure III.



III

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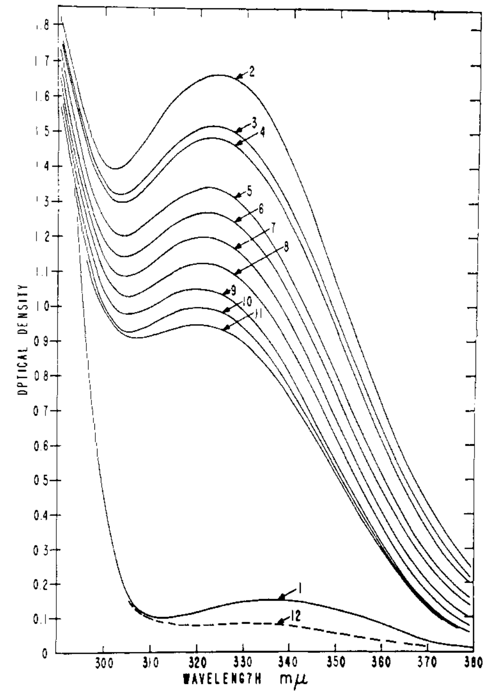


Figure 3. Ultraviolet absorption spectra of 1.03 × 10^{-3} *M* solution of Ph_2CO in Me_2CHOH in a 1-cm square cell, degassed and sealed, at different times: (1) before irradiation (t_0), (2) after 3-min irradiation (t_1) to 72% conversion, (3) after 210 min of dark reaction (past t_1), (4) after 445 min, (5) after 2950 min, (6) after 4580 min, (7) after 8725 min, (8) after 14,730 min, (9) after 28,970 min, (10) after 38,855 min, (11) after 65,800 and 71,000 min (spectrum unchanged, end of the dark reaction, t_∞), (12) after the cell was opened and air was bubbled for 1 hr (the reaction with oxygen is not complete).

There is general agreement with respect to steps 1 and 2.[1,5,11,12,19] Schenck, *et al.*, postulated the intermediate to be isobenzopinacol I or II, formed from two $Ph_2\dot{C}OH$ radicals,[9,10] but left the fate of the short-lived $Me_2\dot{C}OH$ radicals unspecified. Apparently they assume that $Me_2\dot{C}OH$ reacts with Ph_2CO to yield $Ph_2\dot{C}OH$ and Me_2CO. Although both isobenzopinacol I or II and structure III agree with most of the observed properties of the intermediate,[9,10] we must rule out configurations I and II because they cannot be rationalized to agree with the kinetics of the dark reaction reported below and *because, well before the intermediate is completely consumed, the dark reaction stops indefinitely* whenever more than half of the initial Ph_2CO was converted to In during the irradiation (see Figure 3, curve 11). While there is a very logical explanation for the arrest of the dark reaction in the assumption that In has structure III (all Ph_2CO has been consumed), in our opinion, there is no acceptable reason why the reaction, I or II → $Ph_2C(OH)C(OH)Ph_2$, should stop before all the isobenzopinacol has been converted to benzopinacol.

In our proposed mechanism, a concerted-type transformation involving the transition state IV can be rationalized for the rate-determining step (4) in the slow dark reaction between In and Ph_2CO.

Dark-Reaction Kinetics. The rate-determining step (4) gives $d(Ph_2CO)/dt = k_D(In)(Ph_2CO)$ and from the stoichiometry of the reaction one can see that $(In)_0 - (In) = (Ph_2CO)_0 - (Ph_2CO)$ where $(In)_0$ and (In) are the intermediate concentrations immediately after irradiation (at t_1, the beginning of the dark reaction) and at time *t*, respectively, and $(Ph_2CO)_0$ and (Ph_2CO) are the benzophenone concentrations at the same t_1 and *t*, respectively. Replacing $(In) = (In)_0 - (Ph_2CO)_0 + (Ph_2CO)$ in the rate expression and integrating one obtains

$$\ln \frac{[(In)_0 - (Ph_2CO)_0 + (Ph_2CO)](Ph_2CO)_0}{(In)_0(Ph_2CO)} = [(In)_0 - (Ph_2CO)_0]k_Dt$$

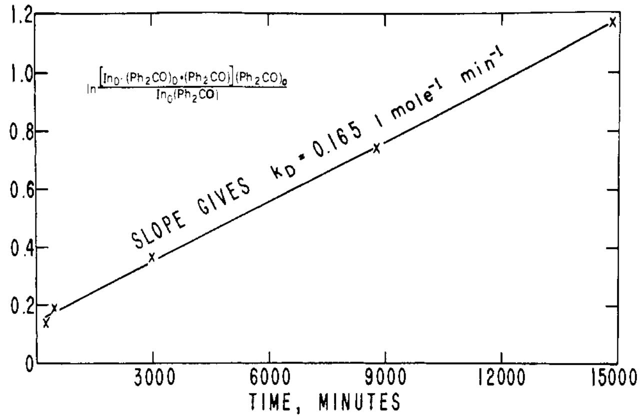
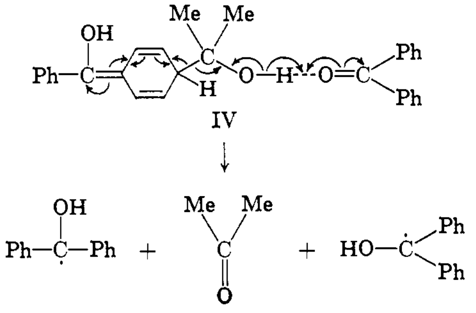


Figure 4. Kinetics of the dark reaction.



Knowing the absorption spectrum of In it is very simple to determine the concentrations $(In)_0$ and $(Ph_2CO)_0$ at the beginning of the dark reaction, as well as (Ph_2CO) at the different intervals, from the absorption spectra in Figure 3. To calculate (Ph_2CO) we measured the absorbancies at three different wavelengths, 310, 320, and 330 mμ, for each curve and used the average value; the three sets of values agreed within 5%, which we estimate the over-all accuracy of the determination to be.

The left-hand side of expression 6 is plotted *vs.* *t* in Figure 4. The graph is an almost perfect straight line, and its slope gives $k_D = 2.75 \times 10^{-3}$ l. mole^{-1} sec^{-1}.

Conclusion

The mechanism and the structure of the intermediate proposed above seem to agree with all observed data. The erratic results reported previously can now be understood since the length of irradiation and variable concentration of Ph_2CO will affect the Ph_2CO → In conversion. Furthermore, if the very long dark reaction is not completed before exposure to air, the quantum yields will depend on the extent of completion.

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For Ph$_2$CO + $h\nu \rightarrow$ In conversions in excess of 50%, the reaction mixture at the end of the dark reaction will contain In, which will ultimately have to react with atmospheric oxygen upon admission of air. Thus, one can easily obtain quantum yields of Ph$_2$CO disappearance ranging from 1 to 2. The only case in which this quantum yield can be close to 2 is if the original Ph$_2$CO + $h\nu \rightarrow$ In conversion is less than 50% and if the dark reaction is allowed to go to completion.

Acknowledgment. We wish to thank William Orvedal, Charles Hurt, and George Mushrush for their assistance in the experimental work and the National Aeronautics and Space Administration for partial support under Grant NsG-603.

The Mechanism of the Photochemical Rearrangement of Lumisantonin[1,2]

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Received January 10, 1967

Abstract: Sensitization studies on the photolysis of lumisantonin together with a reinvestigation of its pyrolysis have yielded results which support a mechanism involving five discreet steps: (1) excitation; (2) intersystem crossing; (3) bond breaking; (4) electron demotion and relaxation to a dipolar state; (5) rearrangement. Photolysis at low temperature in a matrix allowed the trapping of a colored intermediate the lifetime and spectral characteristics of which are consistent with the postulated dipolar state. The possibilities of electron ejection from an excited state or reaction *via* vibrationally excited ground states are discussed and considered to be unlikely in this system.

For several years interest has centered on "ionic" photochemical processes, *i.e.*, those photochemical rearrangements which bear obvious relationships to carbonium ion type reactions. Chapman has formulated this analogy between carbonium ion processes and the photochemical rearrangements of conjugated, unsaturated ketones as the "polar state" hypothesis,[4] in which a positive charge is developed "on the carbon atom β to the carbonyl group in the product controlling state."[4a]

The undeniable utility of the polar state formalism raises a question of the origin of this utility. In carbonyl groups, the lowest excited singlet state is of n $\rightarrow$ π^* type and should have less accumulation of charge at any center than does the ground state, *i.e.*, the excited state should be less, not more, polar than the ground state. Indeed in the n $\rightarrow$ π^* excited state, the oxygen atom of the carbonyl group is electron deficient relative to the ground state and the anticipated reactions (in particular hydrogen abstraction) are more likely to be those of diradicals. Photochemical behavior of this "radical" type is well known for simple ketones[5] and even for some unsaturated ketones.[6–11] That the excited state responsible for these "radical" type of reactions should be the same one in which "ionic" types of rearrangements occur seems, however, unlikely.

Since this work was undertaken, the range of reactions from a diradical type of excited state has been considerably broadened. For example, migrations of hydrogen atoms[12] or even alkyl groups[13] occur, though these processes are essentially unknown in analogous ground-state systems.[14] These additional data, however, make it even less plausible that ionic-type rearrangements can be explained on the basis of triplet diradical intermediates. For example, alkyl migration in a diradical may be an activated process.[13a] If so, alkyl migration in a diradical-like excited state would be particularly unlikely in the condensed phase (where most processes suggestive of dipolar intermediates have been observed) because of the rapidity with which collisions would dissipate any excess (vibrational) energy. In the same vein, typically ionic rearrangements occur in steroids[15]

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