Table V. Kinetics of Isomerization of Triene III by Triethylenediamine at 25.05 + 0.05° in 50% *t*-Butyl Alcohol–50% Dioxane[a] (Run 39)

Time, min	Log (I/I_0)[b]	$k_1 \times 10^5$ sec^{-1}
0	0.696	. . .
120	0.631	1.36
240	0.573	1.35
365	0.518	1.35
613	0.419	1.38
1227	0.247	1.41
1387	0.227	1.35
1658	0.184	1.34
1925	0.143	1.37
	Av	1.36 ± 0.02[c]

[a] Per cent by volume at 25° before mixing. [b] Obtained directly from the ultraviolet spectra chart paper; $\log (I/I_0) = \epsilon cl$ where ϵ = extinction coefficient, c = concentration (*M*), and l = length of light path through the solution (in centimeters). [c] Since the amine concentration was 0.1066 *M*, $k_2 = 1.28 \pm 0.02 \times 10^{-4}$ l. mole^{-1} sec^{-1}. A plot of log (log (I/I_0) *vs.* time gave $k_1 = 1.38 \times 10^{-5}$ sec^{-1} and $k_2 = 1.29 \times 10^{-4}$ l. mole^{-1} sec^{-1}.

was distilled from Linde molecular sieves. Nine 1.00-ml aliquots of the solution were removed and placed in air-tight, stoppered vials. All manipulations were conducted in a dry nitrogen atmosphere. These vials were then immersed in a 25 ± 0.05° constant temperature bath in the dark (114 min after the reactants were dissolved). After an additional 38 min, sampling was begun. Vials were removed from the bath periodically and their entire contents were diluted to 500.00 ml with 95% ethanol and 0.15 ml of of 0.51 *N* sulfuric acid. With a Cary recording spectrophotometer, Model 14M, 2.00-cm cells against a 95% ethanol blank, the intensities of the 308-mμ band (ϵ 23,900) in the ultraviolet spectra of the solutions were measured. The results are recorded in Table V.

The only difference between this procedure and that used with potassium methoxide in methanol is that the base was introduced as a stock solution in the latter case.

Control Experiments. Control experiments showed that between the time a sample was diluted and the ultraviolet spectrum was recorded, less than 0.2% loss of III occurred. This error was neglected since it is below the precision of the entire procedure.

In another control experiment, a solution of 0.0851 g of triene III and 0.1942 g of triethylenediamine was prepared in 20.00 ml of 50% *t*-butyl alcohol–50% dioxane in a dry, nitrogen atmosphere. The solution, sealed under nitrogen, was stored in the dark at room temperature for 12 days (33 half-lives). A 1.00-ml aliquot was removed and diluted to 500.00 ml with 95% ethanol. The ultraviolet spectrum of the resulting solution showed no absorption at all above 280 mμ, but did show the following: $\lambda_{\max}$ 256 mμ (ϵ 1130), 262 (1170), 269 (670), and 273 (300). When compound IV was isolated and purified, it exhibited the following: $\lambda_{\max}$ 256 mμ (ϵ 876), 258 (900), 262 (1020), and 269 (710).

Blank runs without base were carried out in both methanol and 50% dioxane–50% *t*-butyl alcohol. In each blank, autocatalytic decomposition of III was observed, but not until enough points to give a good straight line in the kinetic runs had been obtained. Moreover, no drift in the first-order rate constants was observed in the kinetic runs even long after the autocatalytic decomposition of IV had appeared in the blanks. These facts indicate that the process causing disappearance of III in the blanks was not occurring to a detectable extent in the kinetic runs.

Photoreduction of Pyruvic Acid by Isopropyl Alcohol and *t*-Butyl Alcohol. A Kinetic Study[1]

Douglas S. Kendall and Peter A. Leermakers

Contribution from the Hall Laboratory of Chemistry,
Wesleyan University, Middletown, Connecticut. *Received January 19, 1966*

Abstract: Photoreduction of pyruvic acid has been effected by isopropyl alcohol and by *t*-butyl alcohol, the latter alcohol having been usually considered inert as a hydrogen donor. By quenching experiments, values for the bimolecular hydrogen abstraction rate constants for triplet pyruvic acid with both hydrogen donors have been determined, as well as the approximate value for the unimolecular decay constant in *t*-butyl alcohol.

In the first paper of this series,[2] in addition to discussion of the unusual photodecarboxylation reaction in aqueous solution, we commented on the apparently high efficiency of photoreduction of pyruvic acid when irradiated in a number of various "appropriate" organic solvents. The reduction product was nearly exclusively dimethyltartaric acid, the pinacol formed by coupling of two identical radicals. The purpose of the present investigation was to determine quantitatively the rate constants for the abstraction reaction with two very different hydrogen donors, namely isopropyl alcohol with a very labile α hydrogen, and *t*-butyl alcohol with *no* α hydrogens available, so that if abstraction occurs it is presumably of a methyl hydrogen. (Abstraction from oxygen could also occur, as the methyl C–H and hydroxyl O–H bond energies are similar. However, see ref 3.)

t-Butyl alcohol has traditionally enjoyed the distinction of being inert as a hydrogen donor in photoreduction (especially and specifically that of benzophenone),[4] but our very preliminary observations on the pyruvic acid system[2] and subsequent observations by Cohen[3] and Lwowski[5] in the benzophenone system have indicated that it can indeed donate hydrogen, even though perhaps inefficiently.

The most thoroughly studied photoreduction system has been benzophenone with various donors. Methods of determining rate constants have been chemical[4,6]

---

[1] Photochemistry of α-Keto Acids and α-Keto Esters. V. Part IV: P. A. Leermakers, M. E. Ross, G. F. Vesley, and P. C. Warren, *J. Org. Chem.*, 30, 914 (1965).

[2] P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).

[3] S. G. Cohen and S. Aktipis, *Tetrahedron Letters*, No. 10, 579 (1965).

[4] See, for instance, W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

[5] W. Lwowski and T. W. Mattingly, *ibid.*, **87**, 1947 (1965).

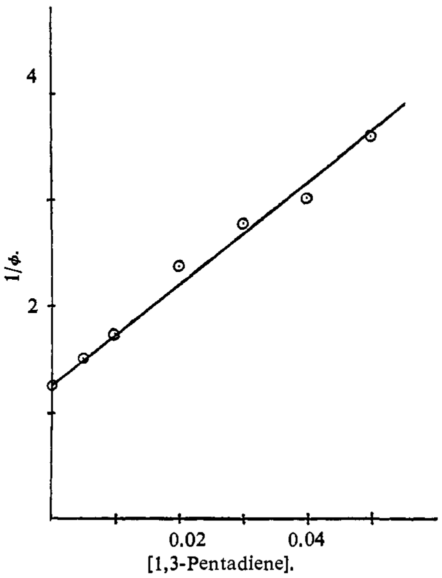


Figure 1. Photoreduction of pyruvic acid in isopropyl alcohol. Variation of reciprocal quantum yield with quencher concentration.

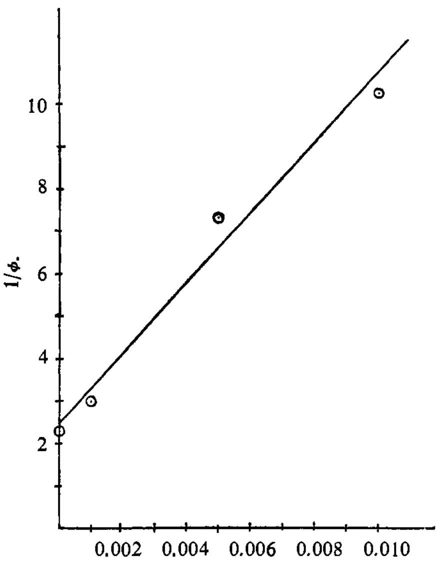


Figure 2. Photoreduction of pyruvic acid in *t*-butyl alcohol. Variation of reciprocal quantum yield with quencher concentration.

(as in the present investigation) and spectroscopic,[7–9] the two methods showing surprisingly good agreement in view of the uncertainties in calculated diffusion rates, and in view of the number of assumptions made. This paper will present our data on the reactivity of triplet pyruvic acid in isopropyl alcohol, a widely studied hydrogen donor, and in *t*-butyl alcohol. An attempt will be made to correlate these data with those for related systems in the existing literature.

Results and Discussion

Equations 1–4 summarize the mechanism believed to hold for photoreduction of a carbonyl compound (RCOR′) by a hydrogen donor (DH). Deactivation of the chemically active excited state both by first-order decay (reaction 2) and by energy transfer to a specific quencher (reaction 3) as well as the critical hydrogen abstraction step (eq 4) are the kinetically significant pathways.

$$\mathrm{RCOR'} + h\nu \longrightarrow \mathrm{RCOR'^*} \tag{1}$$

$$\mathrm{RCOR'^*} \xrightarrow{k_d} \mathrm{RCOR'} \tag{2}$$

$$\mathrm{RCOR'^*} + \mathrm{Q} \xrightarrow{k_q} \mathrm{RCOR'} + \mathrm{Q^*} \tag{3}$$

$$\mathrm{RCOR'^*} + \mathrm{DH} \xrightarrow{k_r} \mathrm{R}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{R'} + \mathrm{D}\cdot \tag{4}$$

The radicals formed in (4) will usually dimerize (to give dimethyltartaric acid in the case of pyruvic acid), and may also cross-couple to some extent.

It has been overwhelmingly established that in general photoreduction reactions of this type proceed *via* the triplet state. Such is certainly the case for pyruvic acid.[2] The variation of quantum yield for reduction with hydrogen donor concentration and quencher concentration follows the well-known rate law (eq 5)[4] where ϕ' is the limiting quantum yield at infinite hydrogen donor concentration.

$$\frac{1}{\phi} = \frac{1}{\phi'} + \frac{k_d}{\phi' k_r[\mathrm{DH}]} + \frac{k_q[\mathrm{Q}]}{\phi' k_r[\mathrm{DH}]} \tag{5}$$

As mentioned in the introduction, our primary concern is the determination of k_r in the pyruvic acid–2-propanol and pyruvic acid–*t*-butyl alcohol systems. Irradiations were carried out at 3660 A under conditions in which all light was absorbed by the system. Graphically plotting $1/\phi$ as a function of quencher (1,3-pentadiene) concentration at constant (neat) hydrogen donor concentration as in Figures 1 and 2 yields values of k_q/k_r in isopropyl alcohol and *t*-butyl alcohol, respectively (Table I). Since $1/\phi$ for isopropyl alcohol was not measured as a function of isopropyl alcohol concentration, ϕ' was not rigorously determined. However, it was clearly near unity and taken as such for purposes of calculation.[10] The value in *t*-butyl alcohol was measured (see Figure 3) as 0.67 (with some margin of error). This is clearly lower than the *triplet* yield for pyruvic acid and is thus somewhat distressing, except that *t*-butyl alcohol is not to be considered a "typical" hydrogen donor in any sense.

Table I

Hydrogen donor	k_q/k_r
Isopropyl alcohol	612
t-Butyl alcohol	5700

The assumption will now be made that quenching of triplet pyruvic acid is diffusion controlled. Although this assumption is probably not correct (*i.e.*, too high)[12]

---

[6] G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).

[7] J. A. Bell and H. Linshitz, *ibid.*, **85**, 528 (1963).

[8] G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

[9] A. Beckett and G. Porter, *ibid.*, **59**, 2039 (1963).

[10] Moore and Ketchum[11] have shown unequivocally that the limiting quantum yield for benzophenone with 2-propanol is 2.0, but this is due to an interesting and fortuitous dark reaction that consumes 1 mole of unexcited ketone per mole of excited ketone. Theoretically, this should not, and obviously does not, happen with pyruvic acid.

[11] W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

[12] R. M. Noyes, *J. Am. Chem. Soc.*, **86**, 4529 (1964).

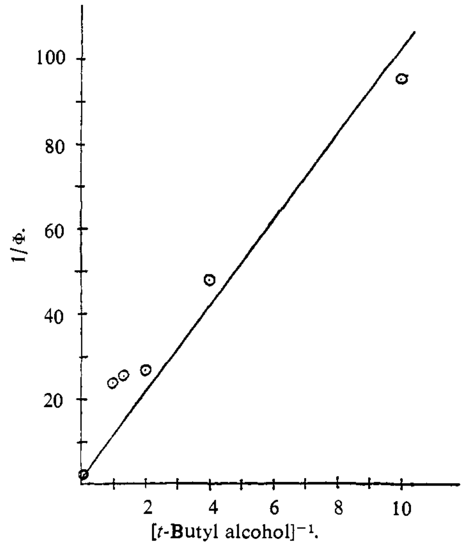
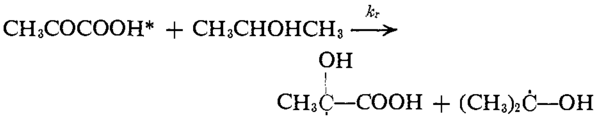


Figure 3. Photoreduction of benzene solutions of pyruvic acid by *t*-butyl alcohol. Variation of reciprocal quantum yield with reciprocal hydrogen donor concentration.

by a factor of 2 or 3, it must be made to make any meaningful correlations with literature values for k_r, all of which assume k_q diffusion controlled. Porter[9] has calculated the bimolecular diffusion-controlled rate constant for neat isopropyl alcohol solvent at 25° using the Debye relation[13] and obtained a value of $3.2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ which he assumed to be k_q for the quenching of benzophenone triplets by naphthalene. This yielded, for the reaction (eq 6), a value of $k_r = 1.28 \times 10^6\ M^{-1}\ \text{sec}^{-1}$. Using the same value for k_q,[14] we calculate, for the reaction (eq 7), $k_r = 5.23 \times 10^6\ M^{-1}\ \text{sec}^{-1}$. Although this is within the same order of magnitude as k_r for benzophenone with the same donor, it is significantly higher since the experimental techniques and conditions (solvent, temperature, assumption of k_q, etc.) are identical. (This may also be compared to Moore's[11] value for reaction 6 of $2.5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, using a rather different experimental approach.)

$$(C_6H_5)_2CO^* + CH_3CHOHCH_3 \longrightarrow (C_6H_5)_2\dot{C}{-}OH + (CH_3)_2\dot{C}{-}OH \qquad (6)$$



$$CH_3COCOOH^* + CH_3CHOHCH_3 \xrightarrow{k_r} CH_3\dot{C}(OH){-}COOH + (CH_3)_2\dot{C}{-}OH \qquad (7)$$

The high reactivity of triplet pyruvic acid toward hydrogen abstraction, nearly fivefold over benzophenone with the same donor, may account for the fact that it is moderately reactive toward *t*-butyl alcohol. Again, using the Debye relation and adjusting for the higher viscosity of *t*-butyl alcohol, k_q is calculated to be $1.3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, which then yields a value of k_r, the rate of hydrogen abstraction from *t*-butyl alcohol by triplet pyruvic acid, equal to $2.3 \times 10^5\ M^{-1}\ \text{sec}^{-1}$. This is *greater* than the rates at which benzophenone abstracts hydrogen from cumene and toluene.[6] From Figure 3, k_d/k_r for the pyruvic acid–*t*-butyl alcohol reaction was determined (in benzene solvent) to be 6.8. From the previously determined value of k_r, the value of k_d, the unimolecular radiationless decay constant for triplet pyruvic acid in benzene–*t*-butyl alcohol mixture, was then calculated to be $1.5 \times 10^6\ \text{sec}^{-1}$. Thus the pyruvic acid triplet is somewhat shorter lived than the benzophenone triplet under roughly the same conditions[4,6] (although values for k_d, as has been pointed out many times in the literature, are not very reproducible, being very sensitive to impurities and other experimentally uncontrollable factors).

In summary, the n,π* triplet state of pyruvic acid is indeed a very reactive species toward hydrogen donors. The reasons for this are not clear, but since it is an α-dicarbonyl compound rather than a simple alkyl or aryl monoketone, the electronic configuration in the excited n,π* state will surely be different, to some extent, apparently with the effect of creating additional radical character on the ketone oxygen. To our knowledge, no quantitative measurements of the type reported in this paper have been reported for other α-dicarbonyl systems.

Experimental Section

Materials. Pyruvic acid (Matheson Coleman and Bell reagent grade) was redistilled under vacuum, stored at ~4°. *t*-Butyl alcohol (Matheson Coleman and Bell reagent grade) was used without further purification. Isopropyl alcohol and benzene (Fisher, reagent grade) were used without further purification. 1,3-Pentadiene (Matheson Coleman and Bell, reagent grade) was redistilled and stored at ~4°.

Apparatus for Quantum-Yield Determinations. The light source for all runs was a Hanovia 450-w high-pressure mercury arc, equipped with a water jacket for cooling. The source and its water jacket were placed in the center of a cyclindrical, rotating device which held the cells equidistant for the source. The filters, Corning 7.60 (transmitting at 3660 A), were taped to the water jacket of the source. The cells, sealed, degassed Pyrex test tubes containing 3 ml of either a sample solution or the standard actinometric solution, received equal illumination because of the holding device's rotation. The entire apparatus was placed in a water bath maintained close to room temperature.

Actinometry. The benzophenone–benzhydrol system described by Moore, Hammond, and Foss[4] was used for actinometry. Both pyruvic acid and benzophenone were 0.3 *M* and quantum yields were derived from the ratio of the quantity of pyruvic acid reacting to the amount of benzophenone reacting; for 0.3 *M* benzophenone and 0.5 *M* benzhydrol in benzene, $\phi = 0.90$ for the disappearance of benzophenone.

Determination of Disappearance of Pyruvic Acid. The disappearance of pyruvic acid was monitored spectrophotometrically. Solutions were diluted 10-fold and their absorbance at 3700 A was measured, both before and after photolysis. The absorbance of the standard benzophenone solutions was measured at 3450 A.

Product Determination for Pyruvic Acid-*t*-Butyl Alcohol Irradiation. A 200-ml solution of 4 ml of pyruvic acid in *t*-butyl alcohol was irradiated for 5 hr in an immersion reactor using a Hanovia 450-w high-pressure mercury arc. The solvent was removed and the product was chromatographed on a silica gel column using petroleum ether (bp 30–60°) and ethyl ether as solvents. Roughly 31% of the pyruvic acid was found to have formed dimethyltartaric acid. Identification was by comparison of the infrared spectrum to that of a known sample.

Acknowledgment. This research has been supported by the National Science Foundation and by a Summer Study Fellowship to Douglas S. Kendall from Wesleyan University. We are indebted to Dr. N. J. Turro for the loan of the "merry-go-round" quantum yield device.

---

(13) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

(14) A reasonable assumption; see G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1149 (1962).