

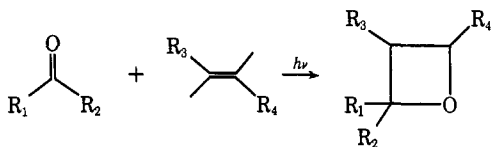
# Quenching of Triplet Phenyl Ketones by Olefins<sup>1</sup>

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**Abstract:** A variety of olefins have been used to quench the type II photoelimination of butyrophenone ( $E_T = 72$  kcal/mol) in benzene. Alkyl-substituted ethylenes are only 0.1–10% as efficient quenchers as are conjugated dienes ( $E_T < 60$  kcal/mol), the most highly substituted ethylenes being the best quenchers. For each *cis*–*trans* pair studied, the *cis*-alkene is the better quencher. The quenching efficiencies of cycloalkenes decrease in the following order:  $C_8 > C_7 \geq C_4 > C_5 > C_6 >$  norbornene. The quenching efficiencies of chloro olefins are greater than those of alkenes, tetrachloroethylene being 30% as effective as a conjugated diene, with *trans*-1,2-dichloroethylene being 2.5 times better than the *cis* isomer. For several olefins, rate constants for quenching of triplet benzophenone ( $E_T = 68$  kcal/mol) and *p*-trifluoromethylbutyrophenone ( $E_T \sim 70$  kcal/mol) are double those for quenching of triplet butyrophenone. These results, together with those reported by other workers, suggest two competitive quenching interactions: charge-transfer (CT) complexing which leads to oxetane formation and olefin isomerization, presumably *via* biradicals; and triplet–triplet energy transfer. Energy transfer predominates for electron-deficient olefins, charge transfer for electron-rich alkenes. CT quenching of excited ketones apparently is a quite general process and probably contributes to triplet quenching by conjugated dienes.

Interest in the Paterno–Büchi reaction<sup>3</sup> has motivated several studies of the reactions of electronically excited ketones with olefins.<sup>4–9</sup> *Cis*–*trans* isomeriza-



tion,<sup>5,7,8</sup> dimerization,<sup>5,9</sup> and rearrangement<sup>10</sup> of the olefin, as well as photoreduction of the ketone, often accompany oxetane formation. The competition between the various processes depends strongly on the structures of both the ketone and the olefin.

The oxetane products are generally believed to arise from 1,4-biradical intermediates<sup>11</sup> formed by addition of an  $n, \pi^*$  excited state of the ketone to ground state olefin. The ketone-sensitized olefin reactions are thought to reflect triplet energy transfer of some kind<sup>4,12</sup> from excited ketone to the olefin. Hence another motive for research in ketone–olefin photointeractions has been interest in mechanisms of triplet energy transfer.

(1) Triplet Energy Transfer. VII. For preliminary communication, see I. E. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, **92**, 5742 (1970).

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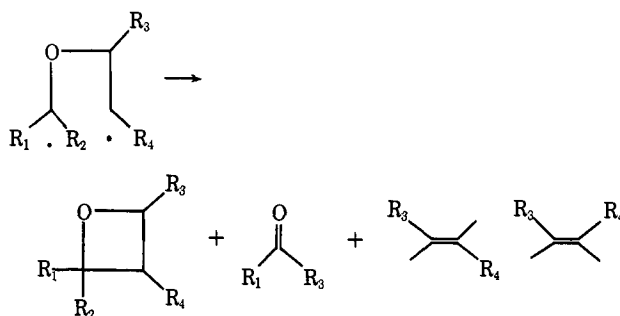
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Triplet excitation energies have not been well established for monoolefins. The onset of the  $S \rightarrow T$  absorption spectrum of ethylene occurs at 82 kcal/mol, which is generally accepted as the energy for a Franck–Condon transition to a planar ethylene triplet.<sup>13</sup> Theory suggests that olefin triplets should be stabilized by twisting about the double bond,<sup>14</sup> and the energy difference between planar ground state ethylene and 90° twisted triplet ethylene has been estimated to be 60–65 kcal.<sup>14–16</sup> Since ketones have triplet energies below 80 kcal/mol, straightforward triplet energy transfer with formation of planar olefin triplets should be endothermic. Both nonvertical energy transfer<sup>17</sup> and Schenck energy transfer<sup>7,18</sup> have been proposed as alternative mechanisms. Recently it has been recognized that the 1,4 biradical (BR) which is thought to lead to oxetanes should also cleave to ground state ketone and isomerized olefin.<sup>8,19</sup> This process amounts to a Schenck mechanism for photosensitized isomerization. How-



ever, sensitized dimerizations and rearrangement of cycloalkenes most likely result from olefin triplets formed by physical energy transfer.

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The fact that ketones with triplet energies greater than 72 kcal/mol sensitize the dimerization of norbornene and do not form oxetanes with it<sup>4,5</sup> suggested that quenching of higher energy ketone triplets by olefins might proceed primarily by physical energy transfer. Consequently, we have studied the quenching of triplet butyrophenone by a wide variety of olefins. Our original idea was that the intermediate triplet energy (74.5 kcal/mol) reported<sup>20</sup> for butyrophenone would favor nonvertical energy transfer, whereas with the previously studied acetone ( $E_T \sim 80$  kcal)<sup>21,22</sup> and benzene ( $E_T = 84$  kcal)<sup>23</sup> vertical energy transfer was more likely. Both our results and those concurrently discovered by others now indicate that triplet energy transfer is not the major quenching reaction.

## Experimental Section

**Materials.** Thiophene-free benzene was further purified by stirring with portions of sulfuric acid until the acid layer remained colorless. After being washed with sodium hydroxide solution and water until neutral, the benzene was dried over calcium chloride and distilled from  $P_2O_5$ . Tetradecane was similarly purified. Simple vacuum distillation of butyrophenone from Matheson Coleman and Bell yielded the highest purity ketone. The quantum yield of acetophenone formation from pure ketone increased slightly with ketone concentration, whereas the opposite effect was taken as a sign of impurity in the ketone.<sup>24</sup> Three samples of butyrophenone from Aldrich Chemical Co., purified by vacuum distillation and recrystallization from pentane, were also used. Differences in triplet lifetime between the different ketone samples were taken into account in determining the  $k_q$  values. *p*-Trifluoromethylbutyrophenone was prepared from propylmagnesium bromide and *p*-trifluoromethylbenzotrile (Columbia Organic Co.). Benzophenone was recrystallized two times from cyclohexane. 2,5-Dimethyl-2,4-hexadiene (Aldrich Chemical Co.) was recrystallized from melt three times at Dry Ice temperature.

Cyclohexene, cycloheptene, cyclooctene, 1,4-cyclohexadiene, norbornene, *cis*- and *trans*-1,2-dichloroethylene, fumaronitrile, methyl acrylate, vinyl acetate, and tetramethylallene were purchased from Aldrich Chemical Co. The following olefins were obtained from Chemical Samples Co.: *cis*-3-hexene (96%), *trans*-3-hexene (99%), *cis*-2-pentene (95%), *trans*-2-pentene (99%), *trans*-2,2,5,5-tetramethyl-3-hexene (99%), and cyclopentene (99%). Trichloroethylene and tetrachloroethylene were purchased from Columbia Chemical Co. 2-Methyl-2-butene, *cis*- and *trans*-4-methyl-2-pentene, 1-pentene, and 2-methyl-1-butene were Phillips Petroleum Co. Pure Grade. The chloro olefins, methyl acrylate, and vinyl acetate were dried and distilled immediately before use; norbornene was sublimed at room temperature and atmospheric pressure; fumaronitrile was recrystallized. All the remaining olefins were purified by preparative gas-liquid chromatography. In addition, most of the olefins were distilled after glpc purification.

Bicyclo[4.2.0]oct-7-ene was prepared by photoisomerizing *cis,cis*-1,3-cyclooctadiene (Aldrich Chemical Co.) to the *cis,trans* isomer and thermally converting this isomer to the bicyclo compound.<sup>25</sup> This olefin was also purified by preparative glpc.

2-Methyl-1-(2,2-dimethylcyclopropyl)propene (1) was prepared by treatment of 2,5-dimethyl-2,4-hexadiene with methylene iodide and a zinc-copper couple in ether.<sup>26</sup> Pure vinylcyclopropane was collected by preparative glpc.

Preparative vapor-phase chromatography of olefins was carried out with a Hewlett-Packard Model 776, Prepmaster, Jr. A 20 ft  $\times$  0.5 in. aluminum column packed with 25% 1,2,3-tris(2-cyanoethoxy)propane on 60-80 Chromosorb P was used.

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**Quenching Experiments.** Butyrophenone and *p*-trifluoromethylbutyrophenone solutions were prepared containing about 0.10 *M* ketone, 0.0025 *M* tetradecane, and known concentrations of olefins. One solution was prepared containing only ketone and tetradecane. Equal aliquots of the solutions were placed in 13  $\times$  100 mm Pyrex tubes with constrictions for sealing. The tubes were degassed by four freeze-thaw cycles ( $<0.005$  Torr) and sealed. Tubes for a particular run were irradiated for the same length of time in a merry-go-round photolysis apparatus. A Hanovia 450-W medium-pressure mercury lamp was used as a light source. The region from 300 to 320 nm was isolated with a 1-cm path of a filter solution containing 0.002 *M*  $K_2CrO_4$  in 1% aqueous solution of  $K_2CO_3$ .

Acetophenone, *p*-trifluoromethylacetophenone, and butyrophenone concentrations were determined relative to tetradecane by glpc. Since all tubes in a particular run were irradiated the same length of time and contained the same concentration of tetradecane, the ratio of areas for ketone to tetradecane in the glpc trace gave the relative quantum yield for the ketone. The above compounds were separated on a 10 ft  $\times$   $\frac{1}{8}$  in. aluminum column packed with 4% QF-1 and 1% Carbowax 20M on 60-80 Chromosorb G at 110-120°. Analyses were performed on a Varian Aerograph Series 1200 gas chromatograph with a flame ionization detector.

Benzophenone solutions were prepared containing 0.03 *M* ketone and varying known concentrations of quencher including one solution with no quencher. The sample tubes were prepared as above. Phosphorescence was measured at 450 and 470 nm upon excitation with 366-nm light using an Aminco-Bowman spectrofluorometer. Emission intensity was read directly from the microphotometer. After the phosphorescence was measured, the tubes were opened and the solutions aerated. The residual signal was measured and subtracted from the original value.

**Quenching Which Leads to Consumption of Butyrophenone.** Solutions were prepared as for quenching runs with 0.10 *M* ketone, tetradecane as internal standard, and sufficient olefin to quench 50-90% of butyrophenone triplets generated. Four or five concentrations of each olefin were used. After irradiation the concentrations of acetophenone and butyrophenone were determined relative to the internal standard by glpc. The fraction of quenching which consumed butyrophenone, FQ, was calculated by the following relationship

$$FQ = B - (A + C)/TQ$$

where  $B$  = mol/l. of butyrophenone consumed,  $(A + C)$  = mol/l. of acetophenone plus cyclobutanol produced, and  $TQ$  = mol/l. of butyrophenone triplets quenched. The sum  $(A + C)$  was calculated by  $A/0.85$  since 85% of the product from the type II reaction yielded acetophenone.  $TQ$  was calculated by subtracting the mol/l. of butyrophenone triplets reacted from the total produced. These last two terms were calculated from the measured values for  $A$  and  $k_q\tau$ .

## Results

**Quenching of Butyrophenone.** Various monoolefins were used to quench the triplet state photoelimination reaction of 0.1 *M* butyrophenone in benzene.<sup>27</sup> The ratio of acetophenone production in the absence to that in the presence of quencher was plotted *vs.* olefin concentration. The resulting Stern-Volmer plots were linear with slopes equal to  $k_q\tau$ , where  $k_q$  is the rate constant for quenching and  $\tau$  is the triplet state lifetime in the absence of quencher. Values of  $\tau$  for the three different butyrophenone samples were determined by quenching with 2,5-dimethyl-2,4-hexadiene. This diene is assumed to quench butyrophenone triplets with a rate constant, in benzene solution, of  $5 \times 10^9 M^{-1} sec^{-1}$ .<sup>28,29</sup> The values of  $k_q$  calculated are listed in Table I. A typical quenching plot is given in Figure 1. The quenching rate constants for the monoolefins are only  $1/10-1/1000$  as large as that of the diene.

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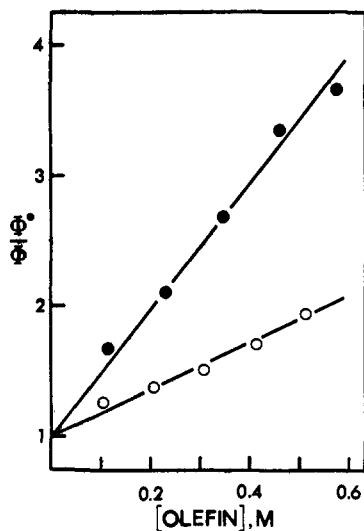


Figure 1. Stern-Volmer plots for quenching of type II reaction of butyrophenone by *cis*-2-pentene (●) and *trans*-2-pentene (○).

It is difficult to obtain reproducible quenching efficiencies for many of the olefins, particularly the cycloalkenes. Simple distillation of commercially obtained

**Table I.** Rates of Quenching of Triplet Butyrophenone by Various Olefins

Olefin	$k_q, 10^7 M^{-1} \text{sec}^{-1}^a$
2,5-Dimethyl-2,4-hexadiene	500 <sup>b</sup>
Fumaronitrile	580
Tetrachloroethylene	145 ± 1
Trichloroethylene	72 ± 5
<i>cis</i> -1,2-Dichloroethylene	16 ± 0.1
<i>trans</i> -1,2-Dichloroethylene	40 ± 2
Methyl acrylate	40
2,3-Dimethyl-2-butene	46 ± 1
2-Methyl-2-butene	14.3 ± 1.5
<i>cis</i> -2-Pentene	5 ± 1.0
<i>trans</i> -2-Pentene	1.9 ± 0.3
<i>cis</i> -3-Hexene	3.6 ± 0.25
<i>trans</i> -3-Hexene	1.1
<i>cis</i> -4-Methyl-2-pentene	0.75
<i>trans</i> -4-Methyl-2-pentene	0.41 ± 0.03
<i>trans</i> -1,2-Di- <i>tert</i> -butylethylene	2.4
2-Methyl-1-butene	2.8 ± 0.25
1-Pentene	0.8
Vinyl acetate	2.0
Vinyl isobutyl ether	8.6
Bicyclo[4.2.0]oct-7-ene	7.5 ± 0.25
Norbornene	3.7 ± 0.1
Cyclopentene	5.2 ± 0.1
Cyclohexene	4.2 ± 1.5
Cycloheptene	7.6
Cyclooctene	8.2
1,4-Cyclohexadiene	14.6
Tetramethylallene	4.6
1	34

<sup>a</sup> Error margins indicate mean deviation from average of duplicate or triplicate runs. No error limits shown when only one run was made. Standard deviations of Stern-Volmer slopes from which  $k_q$  values are derived never exceed 5%. <sup>b</sup> Assumed.

products gives olefins which have high and varying quenching efficiencies, presumably because of traces of dienes formed by autoxidation. Consequently, almost all olefins were measured shortly after being purified by preparative glpc. Such materials afford the lowest  $k_q\tau$  values, which are those we report.

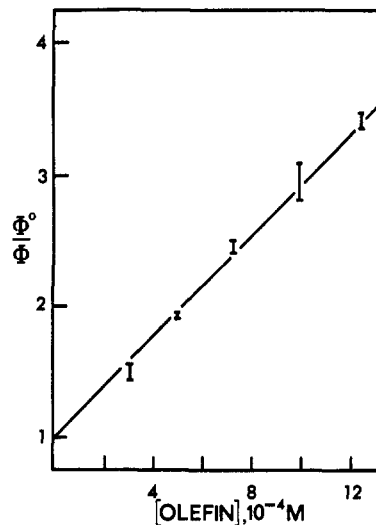


Figure 2. Stern-Volmer plot for quenching of phosphorescence of benzophenone in benzene at 25° by 2-methyl-2-butene.

The last three olefins listed in Table I were studied only briefly in order to get some qualitative knowledge of their quenching efficiencies relative to regular alkenes.

**Quenching of *p*-Trifluoromethylbutyrophenone.** A few olefins were used to quench this substituted butyrophenone, with the results listed in Table II. Although

**Table II.** Quenching of *p*-Trifluoromethylbutyrophenone, Benzophenone, and Butyrophenone Triplets by Monoolefins

Olefin	$k_q \times 10^{-7}, M^{-1} \text{sec}^{-1}$		
	<i>p</i> -Trifluoro- methyl butyro- phenone	Benzo- phenone	Butyro- phenone
Tetramethylethylene		89.5	46
Trimethylethylene	25	36	14.3
<i>cis</i> -2-Pentene	10.6		5.1
Norbornene	4.7	4.0	3.7
Cyclohexene		5.7	4.2

actual  $k_q\tau$  values for a given olefin are about the same for the substituted and unsubstituted butyrophenone, the former has a shorter lifetime, as determined by diene quenching. Therefore olefin  $k_q$  values are larger toward the trifluoromethyl-substituted ketone.

**Quenching of Benzophenone Phosphorescence.** The phosphorescence at room temperature of benzophenone triplet was observed when degassed benzene solutions of the ketone were irradiated at 366 nm. The phosphorescence was measured at 450 and 470 nm in the absence of and in the presence of varying concentrations of quencher and the data were plotted according to the Stern-Volmer relationship. A typical plot is given in Figure 2. The lifetime of benzophenone triplet was determined to be  $6.5 \times 10^{-6}$  sec by quenching with 2,5-dimethyl-2,4-hexadiene, in very good agreement with other measurements.<sup>29,30</sup> The values determined for  $k_q$  for four olefins are given in Table II.

**Quenching Which Leads to Consumption of Butyrophenone.** Previous studies have indicated that oxetanes are produced between monoolefins and ketones which

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**Table III.** Quenching of Butyrophenone Which Leads to Consumption of Ketone

Olefin	FQ
Tetrachloroethylene	0.02
Trichloroethylene	0.02
<i>cis</i> -4-Methyl-2-pentene	0.12
Trimethylethylene	0.05
Cyclohexene	0.40

**Table IV.** Quenching of Some Triplets with Substituted Ethylenes

Quenchee	$E_T$ , kcal/mol	Quencher, $k_q$ , $10^7 M^{-1} \text{sec}^{-1}$			
		$\text{Me}_2\text{C}=\text{CMe}_2$	$\text{Me}_2\text{C}=\text{CHMe}$	$\text{cis-CH}_2\text{CH}=\text{CHC}_2\text{H}_5$	$\text{cis-ClCH}=\text{CHCl}$
Benzene	84 <sup>a</sup>	~500	~500	~500	~500
Acetone	78–80 <sup>b</sup>	~5	~2	~5	~17 <sup>c</sup>
Butyrophenone	72 <sup>d</sup>	46	14	5	16
<i>p</i> -Trifluoromethyl-butyrophenone	70 <sup>d</sup>		25	10	
Benzophenone	68	90, <sup>d</sup> 170 <sup>e</sup>	36, <sup>d</sup> 20 <sup>e</sup>	8 <sup>f</sup>	1.3 <sup>g</sup>

<sup>a</sup> Reference 23. <sup>b</sup> References 19 and 21. <sup>c</sup> D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966). <sup>d</sup> This work. <sup>e</sup> Reference 6. <sup>f</sup> Reference 7. <sup>g</sup> Reference 36.

have about the same triplet energy as butyrophenone.<sup>4</sup> We observed product peaks presumed to be oxetanes in the vpc traces of many of our reactions. The sizes of these peaks generally suggested low quantum yields. The fraction of quenching which leads to consumption of butyrophenone was estimated for five olefins. The products were not isolated. The results in Table III show that, except for cyclohexene, quenching interactions lead at most to small amounts of oxetane formation. Saltiel has reported similar findings for acetophenone-2-pentene.<sup>19</sup> With cyclohexene many product peaks appeared in the vpc trace, presumably due to competing allylic hydrogen abstraction.<sup>5</sup>

## Discussion

**Energy Transfer vs. Complexation.** As mentioned in the introductory section, alkenes can quench triplet ketones by at least two mechanisms. Triplet benzene ( $E_T = 84$  kcal) apparently is quenched completely by energy transfer,<sup>23a</sup> which would be exothermic to all olefins. Triplet acetone ( $E_T = 78$ –80 kcal) apparently is quenched primarily by energy transfer but also partially by some complexation process.<sup>19</sup> Triplet acetophenone ( $E_T = 72.6$  kcal)<sup>31</sup> is presumably quenched largely,<sup>19</sup> and benzophenone ( $E_T = 68$  kcal)<sup>30</sup> probably completely,<sup>32</sup> by chemical complexation to alkenes such as 2-pentene and 3-methyl-2-pentene.

When we first began studying butyrophenone, only its triplet energy in glasses at 77° (74.5 kcal) was known, as well as the fact that its lowest triplet is  $n, \pi^*$  in character. We now know that  $E_T$  for butyrophenone in benzene solution at 25° is only 72.0 kcal,<sup>31</sup> even lower than that of acetophenone. Consequently, in view of Saltiel's work,<sup>19</sup> we would not expect the quenching of triplet butyrophenone by alkenes to consist of very much energy transfer. Table IV summarizes quenching rate constants measured by many different workers. The large decrease in  $k_q$  upon going from benzene to acetone presumably reflects the change from exothermic to mildly endothermic energy transfer. The ensuing

increases in  $k_q$  with decreasing ketone  $E_T$  are totally inconsistent with any kind of energy transfer, vertical or nonvertical, as the major contributor to the quenching process. Therefore, most alkenes must quench triplet butyrophenone predominantly by chemical complexing.

Some energy transfer does occur from triplet butyrophenone to the cycloalkenes. In preliminary experiments we found that propiophenone and butyrophenone

sensitize the dimerization of cyclopentene, the limiting quantum yield being only 1–2%. If triplet cyclopentene dimerizes with the same efficiency (34%) as triplet cyclopentenone,<sup>33</sup> then we can conclude that only ~5% of triplet butyrophenone-cyclopentene interactions yield triplet olefin. Likewise, butyrophenone sensitizes the intramolecular cyclization of 2-norbornene-*endo*-5-methanol,<sup>34</sup> the maximum quantum yield being 8%. Since the efficiency with which the triplet hydroxy olefin cyclizes is not known, we cannot estimate how much quenching by norbornene involves energy transfer. The higher *trans*-*cis* photostationary state of 2-pentene obtained with benzophenone<sup>35</sup> relative to acetophenone<sup>19</sup> as sensitizer suggests that a small percentage of the isomerization sensitized by acetophenone involves energy transfer.

Quenching by the chloroethylenes undoubtedly involves primarily, and perhaps exclusively, energy transfer. The steady decrease in  $k_q$  with decreasing donor triplet energy is probably the best evidence for this conclusion, which Caldwell has reached independently on the basis of deuterium isotope effects.<sup>36</sup> Any reasonable mechanism for complexation between triplet ketones and olefins would predict *decreasing*  $k_q$  values with increasing chlorine substitution, the opposite trend to what is observed. Tetrachloroethylene is in fact almost as effective a quencher as conjugated dienes. Interestingly, *trans*-dichloroethylene is a somewhat better quencher than the *cis* isomer. This difference between geometric isomers parallels that observed for triplet energy transfer from benzene to the 2-butenes.<sup>23</sup> The rapid quenching by fumaronitrile and by methyl acrylate undoubtedly involves energy transfer. Therefore we would assign the triplet energies of the acrylate and the dichloroethylenes as no more than a few kcal above 72, while that of fumaronitrile must be lower than 72 kcal.

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(36) R. A. Caldwell and S. P. James, *J. Amer. Chem. Soc.*, **91**, 5184 (1969).

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(32) R. A. Caldwell, *J. Amer. Chem. Soc.*, **92**, 1439 (1970).

**Complexation. Charge Transfer or Radical Addition?** There is considerable evidence for the formation of 1,4-biradicals from  $n, \pi^*$  ketone triplets and electron-rich olefins.<sup>5,7,11,19</sup> However, the actual quenching mechanism leading to the biradical is not adequately described as a simple radical addition process. There are several pieces of evidence, none of which is unequivocal alone, but which together seem rather convincing.

First, the observed rate constants for reaction of triplet ketones with alkenes are very large, in the range  $10^7$ – $10^9 M^{-1} \text{ sec}^{-1}$ . There is a close parallel between the reactivities of triplet ketones and of alkoxy radicals in both hydrogen atom abstractions<sup>37</sup> and  $\alpha$  cleavages.<sup>38</sup> If the electron-deficient oxygen of the  $n, \pi^*$  ketone triplet adds to the olefin in a radical fashion, as is often pictured,<sup>11</sup> then the  $k_q$  values we have measured should parallel rate constants for addition of alkoxy radicals to olefins. They definitely do not. Alkoxy radicals are unusual in that their rates of addition to olefins are slower than their rates of allylic hydrogen abstraction.<sup>39</sup> Triplet ketones behave just the opposite. Since rate constants for allylic hydrogen abstraction by the *tert*-butoxy radical are on the order  $10^5$ – $10^6 M^{-1} \text{ sec}^{-1}$ ,<sup>39,40</sup> rate constants for alkoxy-radical-like addition of triplet ketones to olefins would be several orders of magnitude lower than our observed  $k_q$  values.

Second, the relative reactivities of various alkenes toward triplet butyrophenone do not parallel the order expected for radical additions. It is well known that 1,2-disubstitution markedly reduces the reactivity of olefins toward radical addition.<sup>41</sup> The expected<sup>42</sup> relative reactivities toward radical addition of some of the alkenes we have studied would be 2-methyl-1-butene > 1-pentene > 2-pentene and 2-methyl-1-butene > 2-methyl-2-butene > 2,3-dimethyl-2-butene. The orders we observe are almost the inverse of the orders predicted for radical addition.

Third, Caldwell has reported that there is no inverse secondary deuterium isotope effect in the benzophenone-sensitized isomerization of 2-butene-2,3- $d_2$ , such as would be expected if a  $sp^2$  carbon were being changed to  $sp^3$  hybridization.<sup>36</sup>

Finally, oxetane formation often is not as stereoselective as would be predicted from the stabilities of the competing biradical intermediates.<sup>4</sup> This fact indicates that the transition state for the product-determining step does not resemble a biradical, just as the relative reactivities of the different olefins indicates that the rate-determining step is not a radical-like reaction.

We conclude, in agreement with Caldwell,<sup>36</sup> that alkene quenching of triplet ketones involves the formation of some sort of complex which can collapse to a 1,4-biradical and that the stability of this complex, not of the biradical, most likely determines the stereoselectivity of oxetane formation. Exactly analogous

suggestions have been made<sup>33,43</sup> for the photocycloadditions of unsaturated ketones.

The nature of the first-formed complex cannot yet be described in great detail. That it has modest charge-transfer character is evidenced by the increase in  $k_q$  as the groups attached to the carbonyl become more electron withdrawing (Table III), by the effects of para substituents on triplet benzophenone  $k_q$  values,<sup>32</sup> and by the relative reactivities of the various alkenes. Thus each alkyl group on the double bond enhances  $k_q$  by a factor of approximately four and the oxygen atoms in vinyl acetate and vinyl isobutyl ether produce even larger rate enhancements.

Unfortunately, it is difficult to make quantitative correlations, primarily because the literature does not provide much information on rates of charge-transfer complex formation. Table V compares our measured

Table V. Probable Charge Transfer Nature of Quenching

Olefin	IP, eV <sup>a</sup>	$K_a, M^{-1}$ <sup>b</sup>	$k_q, 10^7 M^{-1} \text{ sec}^{-1}$ <sup>c</sup>
2,3-Dimethyl-2-butene	8.30	0.1	46
2-Methyl-2-butene	8.68	0.8	14.3
Di- <i>tert</i> -butylethylene	8.73 <sup>d</sup>		2.4
1,4-Cyclohexadiene	8.82 <sup>d</sup>	4.9	14.6
Vinyl isobutyl ether	8.93		8.6
Norbornene	8.95	62	3.7
Cyclohexene	8.95	3.6	4.2*
Cyclopentene	9.01	7.3	5.2
Cycloheptene		12.7	7.6
Cyclooctene		14.4	8.3
<i>cis</i> -4-Methyl-2-pentene	(9.0) <sup>f</sup>	3.1	0.75
<i>trans</i> -4-Methyl-2-pentene	(9.0) <sup>f</sup>	0.7	0.41
<i>cis</i> -3-Hexene	(9.0) <sup>f</sup>	3.9	3.6
<i>trans</i> -3-Hexene	8.95 <sup>d</sup>	1.0	1.1
<i>cis</i> -2-Pentene	9.11	4.3	5.1
<i>trans</i> -2-Pentene	9.06	1.1	1.9
2-Methyl-1-butene	9.12	3.0	2.8
Vinyl acetate	9.19		2.0
1-Pentene	9.50	4.9	0.80

<sup>a</sup> Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 26 (1969).

<sup>b</sup> Association constants for silver-olefin complexes, ref 44. <sup>c</sup> Rate constants for quenching of triplet butyrophenone. <sup>d</sup> D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970). <sup>e</sup> Uncorrected for allylic hydrogen abstraction. <sup>f</sup> Estimated from results in ref d.

$k_q$  values with two admittedly imperfect analogies; olefin ionization potentials, and typical<sup>44</sup> association constants for silver-olefin complexes.

It has been suggested that there ought to be a good correlation between log  $k_q$  values and IP values for charge-transfer quenching processes.<sup>45</sup> Such cannot be generally true, because substituents on the donor cannot sterically hinder photoionization but surely provide varying degrees of steric hindrance to complexation with an acceptor. Figure 3 demonstrates what correlation there is between our  $k_q$  values and olefin IP's. The best straight line for 2,3-dimethyl-2-butene, 2-methyl-2-butene, 2-methyl-1-butene, the 2-pentenes, 1-pentene, and vinyl acetate, all of which would be expected to produce minimal steric hindrance to complexation, actually has a high correlation coefficient. Most

(43) (a) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964); (b) B. D. Challand and P. deMayo, *Chem. Commun.*, 982 (1968).

(44) M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

(45) T. R. Evans, *ibid.*, **93**, 2081 (1971).

(37) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

(38) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

(39) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

(40) (a) D. J. Carlson, and K. U. Ingold, *ibid.*, **89**, 4885, 4891 (1967); (b) C. Walling and V. Kurkov, *ibid.*, **89**, 4895 (1967).

(41) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 127.

(42) A. P. Stefani, L. Herk, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 4732 (1961).

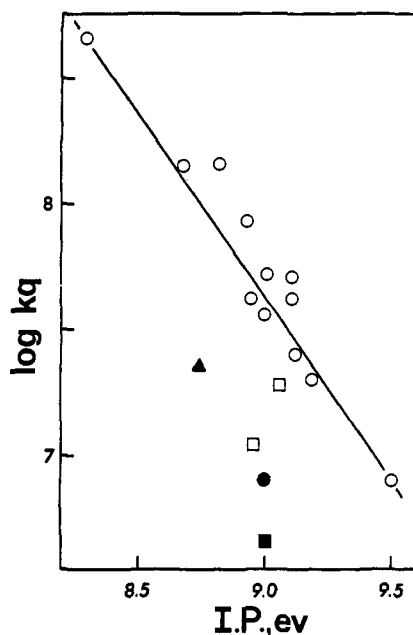
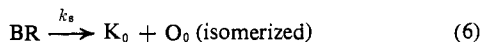
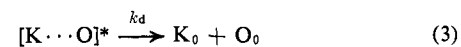
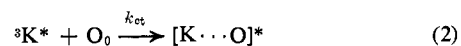
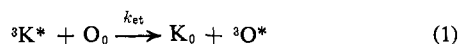


Figure 3. Dependence of rate constants for quenching of butyrophenone on olefin ionization potentials. Data in Table V.

of the points which lie significantly below this line are 1,2-dialkylethlenes containing at least one large alkyl group, in particular di-*tert*-butylethylene ( $\blacktriangle$ ), the 4-methyl-2-pentenes ( $\bullet$  and  $\blacksquare$ ), and *trans*-3-hexene.

**Mechanistic Summary.** Following is a minimum mechanistic scheme for interactions between triplet ketones  ${}^3K^*$  and ground state olefins  $O_0$ .

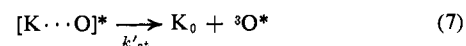


The competition between energy transfer and complexation is determined by the excitation energy of the ketone and by the relative electron deficiency of the  $n, \pi^*$  ketone triplet. Energy transfer is dominant to electron-deficient olefins from all ketones with  $E_T$  values at least as low as 68 kcal. Charge-transfer complexing predominates to electron-rich olefins from ketones with  $E_T$  values  $< \sim 75$  kcal. In general  $k_q$  values such as we have measured equal  $k_{et} + k_{ct}$ .

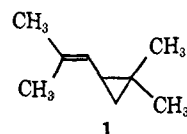
The complex  $[K \cdots O]^*$  might be called an exciplex, but we prefer to call it a CT complex. It would seem desirable to reserve the word "exciplex" for complexes which demonstrate evidence of being *electronically* excited. There is no evidence for exciplex phosphorescence in these systems. There is no evidence that complex formation is reversible. If it were, the observed  $k_q$  values would equal  $k_{ct}(k_{br} + k_d)/(k_{-ct} + k_{br} + k_d)$ . Chapman has reported evidence for such exciplex equilibration in a different cycloaddition system.<sup>46</sup> However, Caldwell's isotope effect studies<sup>36</sup>

(46) O. L. Chapman and R. D. Lura, *J. Amer. Chem. Soc.*, **92**, 6352 (1970).

strongly suggest that  $k_{br} > k_{-ct}$  in ketone-olefin systems. Also, increasing alkyl substitution on the double bond produces opposite effects on  $k_q$  values and on equilibrium constants for complexation with silver ion. Finally, an exciplex might decompose to ground state ketone and triplet olefin; but evidence for such a process in competition with straightforward energy transfer would not be easy to obtain. Complex formation would not occur unless it were somewhat exothermic, so that  $k'_{et}$  must be slower than  $k_{et}$ . Therefore, for reaction 7 to occur,  $k'_{et}$  must be greater than  $k_d + k_{br}$ .



**A Few Special Olefins.** The vinylcyclopropane **1** was studied in order to establish how conjugation with a cyclopropane ring would enhance the quenching ability



of the double bond. **1** is a 2.5-fold better quencher than trimethylethylene. In terms of CT complexing, the cyclopropyl group could surely enhance the donor qualities of the olefin by normal cyclopropylcarbinyl resonance.

Tetramethylallene is twice as effective a quencher as the 1,1-dialkylethylene, exactly what would be expected for two nonconjugated double bonds.

1,4-Cyclohexadiene was studied because of the suggestion that it quenches triplet ketones by some sort of vibrational energy transfer.<sup>47</sup> It is approximately twice as good a quencher as two cyclohexenes, but it does not appear to be much different from other olefins which quench triplet butyrophenone without forming products in high yield. Systems in which decay to ground states of reactants happens to be the major reaction of the CT complex leave few clues as to what is happening. More than one quenching process ascribed to vibrational energy transfer more likely involves charge-transfer complexing.<sup>45, 48</sup>

**Generality of Charge-Transfer Quenching.** Our conclusion that olefins quench triplet ketones by a CT process is hardly startling in light of the many other known CT-quenching processes. Table VI compares some observed quenching rate constants with those predicted from Figure 3. The quenching abilities of amines, sulfides, and thiols lie on the same line as those of the unhindered olefins. However, even if the observed quenching of triplet ketones by benzene consists entirely of charge transfer, the rate<sup>29</sup> fortunately is only 0.1% as large as predicted by benzene's IP. The more rapid charge-transfer quenching of triplet  $\alpha$ -trifluoroacetophenone by substituted benzenes involves the enhanced electrophilicity of the trifluoro-substituted ketone triplet.<sup>49</sup>

In general, one should look at both the triplet excitation energy and the ionization potential of a compound

(47) A. M. Braun, W. B. Hammond, and H. C. Cassidy, *ibid.*, **91**, 6196 (1969).

(48) B. S. Solomon, C. Steel, and A. Weller, *J. Chem. Soc. D*, 927 (1969).

(49) P. J. Wagner and R. A. Leavitt, *J. Amer. Chem. Soc.*, **92**, 5806 (1970).

**Table VI.** Rate Constants for Charge-Transfer Quenching of Triplet Phenyl Ketones

Diene	IP <sup>a</sup>	$k_{ct}, 10^7 M^{-1}$	
		Predicted	Obsd
Triethylamine	7.50	600	350 <sup>b</sup>
Dibutyl sulfide	8.30	50	60 <sup>c,d</sup>
<i>sec</i> -Butylamine	8.70	11	15 <sup>c,e</sup>
<i>n</i> -Butyl mercaptan	9.14	2.5	1.4 <sup>f</sup>
Benzene	9.25	1.8	$\leq 0.002^g$
Isoprene	8.84	7	
1,3-Pentadiene	8.68	13	
Cyclopentadiene	8.57	18	
2,4-Hexadiene	8.48	25	
1,3-Cyclohexadiene	8.40	32	
2,5-Dimethyl-2,4-hexadiene	7.91	150	

<sup>a</sup> References 45 and *d* in Table V; also R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965. <sup>b</sup> P. J. Wagner and A. E. Kempainen, *J. Amer. Chem. Soc.*, **91**, 3085 (1969). <sup>c</sup> Benzophenone. <sup>d</sup> J. B. Gutenplan and S. G. Cohen, *J. Chem. Soc. D*, 247 (1969). <sup>e</sup> S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968). <sup>f</sup> P. J. Wagner and R. G. Zepp, *ibid.*, **93**, 4958 (1971). <sup>g</sup> Reference 29.

to deduce its quenching potential. In this regard, the behavior of conjugated dienes is both interesting, since their IP's are appreciably lower than those of monoolefins, and important, since dienes are widely used to monitor triplet yields and lifetimes. Since the original submission of this paper, two groups of workers<sup>50,51</sup> have ascribed the previously reported diene quenching of alkanone fluorescence,<sup>52</sup> which is accompanied by

(50) N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93**, 4056 (1971).  
 (51) R. R. Hautala and N. J. Turro, *ibid.*, **93**, 5595 (1971).  
 (52) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1793 (1970).

cycloadduct formation,<sup>50,53</sup> to charge-transfer quenching of  $n, \pi^*$  singlets. Interestingly, one line correlates the singlet quenching rates of both dienes and monoolefins as a function of quencher IP.<sup>50</sup> Moreover, actual  $k_q$  (singlet) values for monoolefins are very similar to the  $k_q$  (triplet) values we report here. Therefore, charge-transfer quenching of ketone triplets undoubtedly competes with electronic energy transfer for dienes with especially low IP's, as indicated by the predicted rate constants in Table VI for charge-transfer quenching by commonly used dienes. The very low quantum yield oxetane formation observed upon irradiation of benzophenone with 2,3-dimethyl-1,3-butadiene<sup>54,55</sup> and other dienes<sup>55</sup> very likely involves such a process. Figure 3 would predict a rate constant for quenching of triplet ketones by 2,3-dimethyl-1,3-butadiene on the order of  $10^8 M^{-1} \text{sec}^{-1}$ , much larger than the  $10^6 M^{-1} \text{sec}^{-1}$  value estimated.<sup>55</sup> However, that estimate must be low because it assumed no radiationless decay due to reversible complexation.

Finally, we can note that only  $\sim 1\%$  CT quenching is expected to compete with triplet energy transfer to 1,3-pentadiene, so that triplet counting by that diene<sup>56</sup> should not be endangered.

**Acknowledgment.** Preliminary work was performed by Mr. John Barber and supported by Research Corporation. A National Science Foundation grant also provided assistance.

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 (56) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965)

## Intermolecular Hydrogen Transfer Reactions in the Mass Spectra of Dialkyl Malonates

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**Abstract:** Intermolecular hydrogen transfer reactions of dialkyl malonates have been investigated under conditions of low-pressure mass spectrometry. Extensive deuterium labeling, which was exhaustive in the case of dimethyl, diethyl, di-*n*-propyl, and diisopropyl esters, aided in determining the sources of hydrogen transferred in the formation of  $M + H$ , and the identities of the most effective proton donors. It was concluded that the high reactivity which is characteristic of this class of compounds is due mainly to ions which bear labile hydrogens bound to oxygen, including  $\text{ROC}(\text{OH})\text{CH}_2^+$ ,  $\text{HOCOCH}_2\text{C}(\text{OH})_2^+$ , and  $\text{ROCOCH}_2\text{C}(\text{OH})_2^+$ . No evidence was found for fragment ions formed by decomposition of the  $M + H$  species.

Intermolecular hydrogen transfer reactions which lead to protonated molecular ions ( $M + H$ ) are common processes in low-pressure organic mass spectrometry. Examples of their occurrence and recognition of their dependence upon pressure are available in the early literature, and include aliphatic ethers,<sup>1</sup> nitriles,<sup>2,3</sup> amines, and other heteroatom-containing

molecules.<sup>1</sup> The utility of these ions in establishment of molecular weight was recognized by McLafferty,<sup>1</sup> but their mechanisms of formation in most cases have remained obscure in spite of the development of gas-ous ion-molecule chemistry.<sup>4</sup> Relatively few studies

(1) F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957).

(2) J. H. Beynon, G. R. Lester, R. A. Saunders, and A. E. Williams, *Trans. Faraday Soc.*, **57**, 1259 (1961).

(3) F. W. McLafferty, *Anal. Chem.*, **34**, 26 (1962).