kcal, which is sufficient to account for the observed emission. In addition, this mechanism

$$\mathrm{NiO} + \mathrm{CO} \longrightarrow \mathrm{Ni(g)} + \mathrm{CO_2} \qquad (1)$$

$$\mathrm{Ni(g)} + \mathrm{O_3} \longrightarrow \mathrm{NiO^*} + \mathrm{O_2} \qquad (2)$$

explains the observed extremely slow decay of the light intensity by regeneration of NiO*. A further study of the iron carbonyl–ozone reaction revealed that a similar effect could also be obtained from FeO* at a much greater concentration of carbon monoxide.

The results reported here may explain the light emission and initial fast reaction observed by other investigators studying the carbon monoxide–ozone system.[3]

[3] J. Pressman, L. M. Arin, and P. Warneck, Final Report, Contract No. CPA 22-69-36, U. S. Public Health Service, NAPCA-CRC.

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Triplet Ketone–Olefin Interactions: Energy Transfer, Charge Transfer, or Radical Addition?

Sir:

The interactions of ketone triplets with olefins are of widespread interest;[1–7] nonetheless, no comprehensive study of the effects of olefin structure on the rate constants for quenching of triplet ketones has yet been reported. We have performed such a study and report here those results most pertinent to the question of the mechanism for the quenching interaction.

There seems little doubt that triplet benzene (E_T = 84 kcal) is quenched by olefins *via* very efficient electronic energy transfer.[8] This behavior is reasonable, since the vertical triplet excitation energy of ethylene is now generally accepted to be 82 kcal.[9,10] Triplet acetone (E_T = 78–80 kcal), on the other hand, seems to interact with 2-pentene by two competitive mechanisms: electronic energy transfer and revertible chemical addition.[3] The olefin apparently undergoes sensitized cis–trans isomerization both from its triplet and by cleavage of a metastable adduct. Kinetic evidence suggests that triplet acetophenone[3] (E_T = 73.5 kcal) and triplet benzophenone[2] (E_T = 69 kcal) sensitize the isomerization of olefins predominately *via* formation and fragmentation of metastable adducts.

The intermediacy of 1,4 biradicals in these ketone–olefin interactions is strongly suggested by the kinetic evidence for an intermediate which can fragment to ground-state ketone and (isomerized) olefin and by the competitive, nonstereospecific formation of oxetanes. In fact, most authors have suggested that the phenyl ketone triplets add directly to olefins to yield biradicals. Our results add support to the developing consensus that the triplets of phenyl ketones ($E_T <$ 75 kcal) interact with acyclic olefins primarily by formation of a metastable adduct. However, we feel that a charge-transfer complex (or exciplex) precedes the biradical since the effects of olefin and ketone structure on quenching rate constants are inconsistent with radical-like additions.

We have measured the efficiency with which various olefins[11] quench the type II photoelimination of butyrophenone in benzene.[12] Table I lists the Stern–Volmer slopes and k_q values calculated from them. Table II compares our results with those in the literature for the k_q values of dichloro-, dialkyl-, trialkyl-, and tetraalkylethylenes toward various triplets.

Table II reveals a sharp decrease in quenching rates for the alkenes in going from benzene to acetone, as would be expected when energy transfer becomes endothermic or nonvertical. However, the further decreases in triplet energy of the phenyl ketones are accompanied by *increased* values of k_q. This reversal effectively rules out energy transfer as the rate-determining quenching process.

The effects of varying olefin structure on k_q (contained in Table I) do not parallel those on known rates of electrophilic free-radical additions.[13] For example, 1,1-dialkylethylenes are no better quenchers than 1,2-dialkylethylenes, and di-*tert*-butylethylene is no worse a quencher than *trans*-4-octene.

It has been established that alkoxy radicals serve as excellent models for the hydrogen abstraction reactions of n,π* ketone triplets.[14,15] The k_q values in Tables I and II are several orders of magnitude larger than what would be expected for alkoxy radical-like additions.[16] The 10–20-fold larger k_q values of the phenyl ketones compared to acetone do not parallel the similarity in reactivity displayed by these ketones in hydrogen abstraction reactions.[17] However, the electron-withdrawing phenyl groups would be expected to increase the electrophilicity of the n,π* triplet states.

We suggest that the sum of all available evidence is most consistent with the primary interaction between ketone triplet and olefin being formation of a charge-transfer complex, whenever energy transfer is so endothermic as to be negligibly slow. This complex presumably collapses to a biradical, the structure of which is determined by the orientation of ketone and olefin in the complex. The lack of predictable stereoselectivity in oxetane formation[1] is further testimony to the presence

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(11) All olefins were purified by preparative vpc; other methods do not remove trace impurities which increase the apparent quenching efficiency of many olefins, especially the cycloalkenes.

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(16) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1965); C. Walling and V. P. Kurkov, *ibid.*, **89**, 4895 (1967).

(17) For example, compare P. J. Wagner, *ibid.*, **88**, 5672 (1966), with N. C. Yang and R. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).

Table I. Rate Constants for Quenching of Triplet Butyrophenone[a] by Various Olefins

Olefin	$k_q\tau$[b]	k_q, 10^7 M^{-1} sec^{-1} [c]
$CH_2{=}CH{-}CH{=}CH{-}CH_3$	580	500
$(CH_3)_2C{=}C(CH_3)_2$	52.5	46 ± 3
$(CH_3)_2C{=}CH{-}CH_3$	15.0	14 ± 1.5
$CH_2{=}C(CH_3)CH_2CH_3$	3.2	2.8 ± 0.2
cis-$CH_3CH{=}CHCH_2CH_3$	4.0	3.0 ± 1.0
trans-$CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3$	1.25	1.1 ± 0.2
trans-*t*-BuCH=CH*t*-Bu	1.9	2.4
$CH_2{=}CHCH_2CH_2CH_3$	0.90	0.8
Cyclopentene	6.1	5.2 ± 0.1
Norbornene	3.4	3.7 ± 0.1
Cyclohexene	4.2	4.2 ± 1.5
1,4-Cyclohexadiene	11.6	14.6
cis-ClCH=CH—Cl	18	16 ± 0.1
$Cl_2C{=}CHCl$	82	72 ± 5
$Cl_2C{=}CCl_2$	165	145 ± 1

[a] 0.10 *M* butyrophenone in benzene at 25°, irradiated at 3130 Å. [b] Generally the average of two or more runs. [c] Errors represent mean deviation from average, none shown for single runs.

Table II. Quenching Rates of Select Olefins toward Various Energy Triplets

Quenchee (E_T)	Quencher, k_q, 10^7 M^{-1} sec^{-1}: RCH=CHR	$Me_2C{=}CHMe$	$Me_2C{=}CMe_2$	ClCH=CHCl
Benzene (84)[a]	~500	~500	~500	~500
Acetone (78–80)[b,c]	~1	~2	~5	
PhCOPr (74.5)[d]	1–5	14	46	16
$PhCOCH_3$ (73.5)[b]	1–2			
PhCOPh (68.5)	8[e]	20[f]	170[f]	1.3[g]

[a] See ref 8. [b] Reference 3. [c] Reference 7. [d] This work. [e] Reference 2. [f] N. C. Yang, R. Loeschen, and D. Mitchell, *J. Amer. Chem. Soc.*, **89**, 5465 (1967). [g] Reference 4.

of an intermediate besides the biradical. Such π complexing to electrophilic species is a characteristic reaction of olefins and is thought to occur in the photocycloaddition reactions of α,β-unsaturated cyclic ketones.[18]

Two further observations deserve attention. The chloroethylenes are much better quenchers of butyrophenone than are the analogous alkylethylenes. Such behavior is consistent only with energy transfer being the major quenching process, since both C–T complexing and radical addition would be slowed by increasing chloro substitution.[19]

The behavior of the cyclic olefins is especially interesting in that they are all significantly better quenchers than are the *cis*-1,2-dialkylethylenes. Furthermore, ketones with triplet excitation energies >73 kcal sensitize dimerization of the strained cycloalkenes.[1] Our study of the dependence of butyrophenone-sensitized cyclopentene and norbornene dimer quantum yields on olefin concentration suggests that as much as one-half of the total quenching may involve energy transfer. Unless the dimerization somehow does not involve olefin triplets, we must conclude that triplet energy transfer to the strained cycloalkenes is considerably faster than to the unstrained alkenes. This behavior is reasonable only if the π,π* triplets undergo rehybridization to an sp^3-like configuration at the olefinic carbons.[20]

All the alkenes and cycloalkenes seem to give small amounts of oxetanes. With none of the olefins we studied does product formation (loss of butyrophenone) account for more than 20% of the total quenching, except for cyclohexene, where photoreduction[1] products are evident. If a charge-transfer complex is indeed formed, the efficiency with which it collapses to a biradical and the partitioning of the biradical are obviously subtle functions of olefin structure. Therefore it is not possible to correlate oxetane yields with the mechanism of quenching.

Finally, the quenching efficiency of 1,4-cyclohexadiene is not out of line with that displayed by many other olefins, so that we question the necessity of invoking a new mechanism such as vibrational quenching.[5]

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(19) Caldwell has reached the same conclusion from a study of isotope effects.[4] Moreover, dichloroethylene quenches triplet benzophenone ($E_T \sim 69$ kcal) only 1/20th as fast as it quenches triplet butyrophenone.

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The Total Synthesis of an Unsymmetrical Pentacyclic Triterpene. DL-Germanicol

Sir:

For some time a portion of the effort of these laboratories has been directed toward the development of reaction patterns suitable for the total synthesis