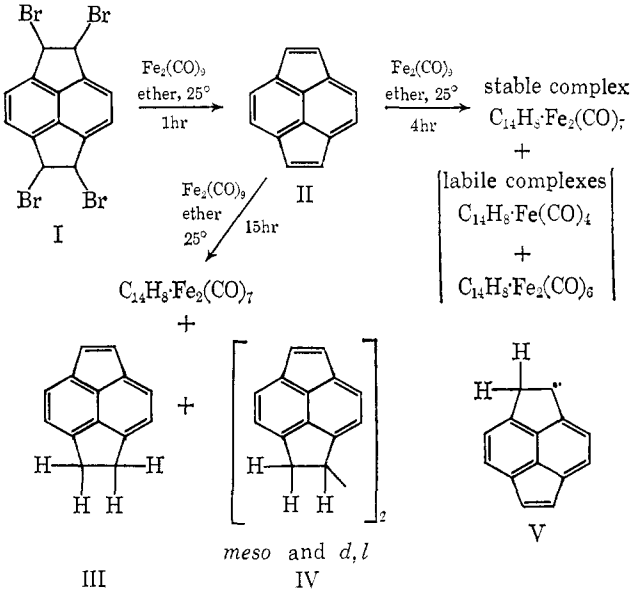
to no deuterium incorporation in either III or IV—a fact suggesting the ethereal solvent as the hydrogen source.

While treatment of pyracylene itself with diiron nonacarbonyl for 15-hr periods under similar conditions produces the $C_{14}H_8 \cdot Fe_2(CO)_7$ complex and reduction products III and IV, a mixture containing only organic iron carbonyl complexes is observed if the reaction is allowed to proceed just 4 hr. Preparative thin layer chromatography separates this mixture into two fractions, the fastest moving fraction containing a single component, the previously observed $C_{14}H_8 \cdot Fe_2(CO)_7$ complex. The second fraction consists of several very labile complexes, two major components having molecular formulas $C_{14}H_8 \cdot Fe(CO)_4$ and $C_{14}H_8 \cdot Fe_2(CO)_6$ by mass spectrometry.[7] Whereas the $C_{14}H_8 \cdot Fe_2(CO)_7$ complex remains unchanged when subjected for 20-hr periods to the reaction conditions of Scheme I, experiments with the mixture of iron tetracarbonyl and diiron hexacarbonyl complexes indicate that one or both of these unstable materials is responsible for reduction products III and IV. Upon standing in organic solvents, decomposition of the complexes occurs generating the observed products.

Scheme I. Reaction of Pyracylene with Diiron Nonacarbonyl



The anhydrous experimental conditions and the absence of deuterium in III and IV when D_2O is used in workup suggest the absence of proton-abstracting intermediates such as the free pyracylene radical anion or dianion. Furthermore, the absence of higher oligomers indicates the absence of free pyracylene radical anion. A most reasonable explanation for the formation of reduction products III and IV requires that in the intermediate pyracylene–iron carbonyl complex(es) involved in the reduction, the highest occupied orbital having primarily metal character and the lowest lying vacant orbital having mainly ligand character be of similar energy. Thus, a thermally accessible triplet state could be realized by the transfer of an electron from the highest occupied "metal orbital" to the vacant lowest lying "ligand orbital."[8] Hydrogen abstraction from solvent by this triplet species would produce radical V, either free or, more likely, complexed with iron.[9] Hydrogen abstraction from solvent by V would produce III, whereas an attack on a pyracylene molecule, with subsequent hydrogen abstraction from solvent, would lead to the dimeric product IV. This example represents the first reported case of a hydrocarbon ligand reduction by an iron carbonyl.

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(7) The nmr spectrum of this second thin layer fraction is consistent with reasonable structures for complexes having these molecular formulas. The mass spectrum shows peaks at *m/e* 344, 316, 288, 260, 232, 176, and 150 for the iron tetracarbonyl complex and peaks at *m/e* 456, 428, 400, 373, 344, 316, 288, 260, 232, 176, and 150 for the diiron hexacarbonyl complex. However the extreme lability of these complexes has thus far precluded their separation and complete characterization.

(8) For a discussion of current theories regarding the bonding in arene and olefin–metal carbonyl complexes see F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, Chapters 26–28.

(9) The absence of high polymers suggests that these radicals (*i.e.*, V) are not free, but are bonded in some manners to iron.

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Barry M. Trost,[10] G. Michael Bright
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
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Kinetics of Photoreduction of Aromatic Ketones by Primary, Secondary, and Tertiary Aliphatic Amines

Sir:

We have previously studied the kinetics of photoreduction of benzophenone by a primary amine, 2-butylamine, in benzene and have reported[1] values for k_{ir} and k_d, the rate constants for interaction of the excited triplet ketone with the amine and that for decay of the triplet, respectively. We were unable to carry out such studies with secondary and tertiary amines because of formation of light-absorbing products. This difficulty was avoided in aqueous medium, in which secondary and tertiary amines were very effective photoreducing agents.[2] Kinetic constants have now been determined for photoreduction of the 4-benzoylbenzoate anion by the three classes of amines in aqueous medium. Reaction with tertiary amines is exceedingly rapid.

Solutions of 0.10 *M* 4-benzoylbenzoic acid, 0.12 *N* NaOH, and 0.050–1.0 *M* amine in 1:1 water–pyridine were degassed and irradiated under argon in Pyrex tubes on a turntable with a G.E. H-85 W-A3 lamp. Photoreduction of the ketone was followed by measurement at 338 nm of the absorbance of aliquots diluted with acidified 2-propanol. Rates of photoreduction of 0.10 *M* ketone by 1.0 *M* amine in the same medium were determined as a function of concentration (0.0050–0.080 *M*) of a quencher, naphthalene. Linear plots of inverse rate against inverse concentration of amine, and of inverse rate against concentration of naphthalene, led to values of k_{ir}/k_d and k_q/k_{ir}. Some results are summarized in Table I. Data for photoreduction of this ketone and of benzophenone by 1 *M* 2-propanol are included.

(1) S. G. Cohen and H. M. Chao, *J. Am. Chem. Soc.*, **99**, 165 (1968).
(2) S. G. Cohen, H. M. Chao, and N. Stein, *ibid.*, **90**, 521 (1968).

Table I. Photoreduction of 0.10 M 4-Benzoylbenzoate anion, BCO_2^-, and Benzophenone, B, in 0.12 N NaOH in 1:1 Water–Pyridine

Ketone	Amine	k_d/k_{ir}, M	k_q/k_{ir}	k_{ir},[a] M^{-1} sec^{-1}	k_d, sec^{-1}
BCO_2H	2-$BuNH_2$	0.103	44	6.3×10^7	6.4×10^6
BCO_2H	2-BuNHMe	0.030	16	1.6×10^8	4.8×10^6
BCO_2H	2-$BuNMe_2$	0.011	2.7	9.4×10^8	10.2×10^6
BCO_2H	Et_3N	0.021	4.2	6.0×10^8	12.7×10^6
BCO_2H	2-PrOH	1.65	1730	1.7×10^6	2.8×10^6
B	2-PrOH[b]	0.102	2020	1.4×10^6	1.5×10^5

[a] Values of k_{ir} are calculated from k_q/k_{ir}, with values of k_q, 2.5–2.9 $\times 10^9$ M^{-1} sec^{-1}, calculated from the Debye equation and measured viscosities. [b] No alkali was added to the 1:1 water–pyridine medium.

The value of k_{ir} for interaction of the triplet of the carboxy ketone with 2-butylamine in this aqueous medium is 6.3×10^7 M^{-1} sec^{-1}, slightly less than that for benzophenone–2-butylamine in benzene,[1] 1.8×10^8 M^{-1} sec^{-1}, based on $k_q/k_{ir} = 33$ and $k_q = 6 \times 10^9$ M^{-1} sec^{-1}. The values of k_{ir} rise from primary to secondary to tertiary amine. For the tertiary amines $k_q/k_{ir} = 3$, a very low value. Interaction of the ketone triplet with the nonbonding electrons of tertiary aliphatic amines, $k_{ir} = 8 \times 10^8$ M^{-1} sec^{-1}, may be essentially diffusion controlled, particularly if a small steric probability factor lowers the value slightly. This order of increasing reactivity is that of the decreasing ionization potential[3] of the amines, and is consistent with and supports our proposal[1,4,5] that the reaction proceeds *via* a rapid charge-transfer interaction, which leads to partial quenching (−1a) and partial reduction (1b).

$$Ar_2C{=}O^*\ (T_1) + CH_3CH_2NR_2 \xrightarrow{k_{ir}} [Ar_2\dot{C}{-}O^-\ CH_3CH_2\overset{+\cdot}{N}R_2] \quad (1)$$
$$\text{(−1a)}\swarrow \qquad \text{(1b)}\downarrow$$
$$Ar_2C{=}O\ (S_0) + CH_3CH_2NR_2 \qquad Ar_2\dot{C}{-}OH + CH_3\dot{C}HNR_2$$

Reaction of the carboxy ketone triplet with 2-propanol is very much slower: $k_q/k_r = 1.7 \times 10^3$, $k_r = 1.7 \times 10^6$ M^{-1} sec^{-1}. It is similar to that of benzophenone with 2-propanol in this medium, indicating no special effect of the carboxylate group on reactivity. The carboxylate group does lead to high rate of triplet deactivation, $k_d = 2.8 \times 10^6$ sec^{-1} as compared with 1.5×10^5 sec^{-1} for benzophenone, both measured in the 2-propanol system; the values of k_d for the carboxy ketone appear to be even slightly higher in the presence of the amines. Other less reactive ketones which we have studied, *p*-aminobenzophenone[4] and fluorenone,[5] have lower values for k_{ir} with triethylamine, 1×10^7 and 2×10^7 M^{-1} sec^{-1}, respectively.

The product of photoreduction of the carboxy ketone by the amines in the alkaline aqueous medium is the 4-carboxybenzhydrol, formed by disproportionation of the ketyl radical ions. The quantum yield for photoreduction of the carboxy ketone by the tertiary amines in the aqueous system is 0.7, corresponding to 1.4 for formation of the ketyl radical. A second reducing moiety is transferred from the amine-derived radical to ground-state ketone (eq 2), leading either to a vinylamine, which has been characterized in the photoreduction of benzophenone by triethylamine in benzene,[6] or to a charged species, $CH_3CH{=}\overset{+}{N}R_2$, both of which may lead in the aqueous system to the carbonyl compound and secondary amine, which have been isolated[2] (eq 2 and 3).

$$Ar_2C{=}O + CH_3\dot{C}HNR_2 \quad (2)$$
$$\downarrow \qquad \searrow$$
$$Ar_2\dot{C}{-}OH + CH_2{=}CHNR_2 \qquad CH_3\overset{+}{C}HNR_2 + Ar_2\dot{C}{-}O^-$$
$$\downarrow H_2O \qquad H_2O \downarrow$$
$$CH_3CH{=}O + HNR_2 \quad (3)$$

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(4) S. G. Cohen and J. I. Cohen, *J. Am. Chem. Soc.*, **89**, 164 (1967); *J. Phys. Chem.*, 72, 3782 (1968).

(5) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Letters*, 5353 (1968).

(6) N. Stein and S. G. Cohen, unpublished results.

Saul G. Cohen, Nina Stein
Department of Chemistry, Brandeis University
Waltham, Massachusetts 02154
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