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Relative Rate of Hydrogen Abstraction by the Triplet State of Phenanthraquinone

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The ability of the triplet state of some carbonyl compounds such as benzophenone to abstract hydrogen from a suitable substrate is well known and recognized as a critical step in the photoreduction of the carbonyl compound.1) The triplet state of the carbonyl compound is, therefore, radicalic in nature, and it is interesting to compare the relative ability of hydrogen abstraction by the triplet state with the case of other radicals.

By a preliminary experiment we found the great ability of photo-activated phenanthraquinone to abstract hydrogen from the hydrogen donor. The great ability to hydrogen abstraction of the photo-activated species is reflected in the fact that phenanthraquinone can be reduced easily when it is irradiated in benzene. Phenanthraquinone has a maximum absorption at 410—420 mμ, it may be correspond to the $n\rightarrow\pi^*$ absorption band because it can be reduced even if it is irradiated with visible light (any light in the UV region was excluded by ordinary glass and a thick water layer, 150 mm).

Since the rate of hydrogen abstraction is strongly inhibited in the presence of oxygen, it seems resonable to deduce that the triplet state of phenanthraquinone is responsible for the hydrogen abstraction.

The rate of the disappearance of phenanthraquinone dissolved in a large excess of a suitable substrate when it is irradiated follow the first-order kinetics for the concentration of phenanthraquinone.

TABLE 1. RELATIVE RATE OF HYDROGEN ABSTRACTION BY THE TRIPLET STATE OF PHENANTHRAQUINONE

Substrate	20°C	40°C	60°C
Benzene	0.33	0.41	0.44
Toluene	1.00	1.42	1.85
Ethylbenzene	1.27	1.48	2.25
Cumene	2.33	2.65	2.36
t-Butylbenzene	0.42	0.48	0.53
Diethyl ether	3.44	3.59	—
Dioxane	2.47	2.48	2.58
Tetrahydrofuran	1.78	2.96	3.06
Methanol	0.92	1.14	1.32
Ethanol	2.16	2.42	2.75
2-Propanol	5.03	2.20	5.00

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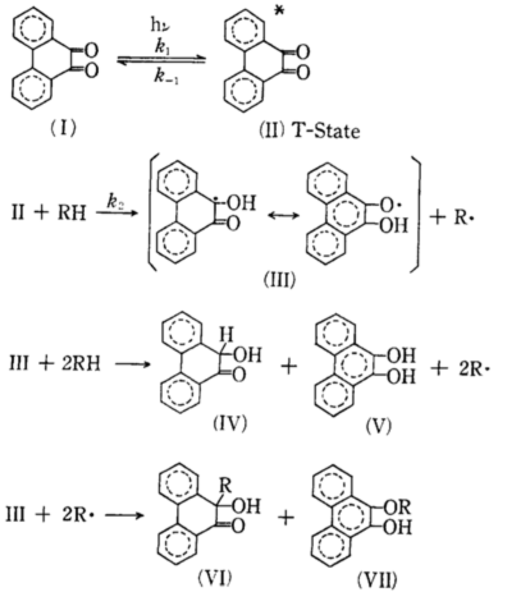
1) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **86**, 3902 (1964); G. S. Hammond and N. Turro, *Science*, **142**, 1541 (1963).

Therefore, the relative rate of hydrogen abstraction was determined from the plot of log(phenanthraquinone) against the time. Representative examples are shown in Fig. 1, while the relative rates obtained are tabulated in Table 1.

If we assume the steady-state concentration for the triplet state of phenanthraquinone, the pseudo-first-order kinetics can be formulated as follows:



$$\frac{d[I]}{dt} = -\frac{k_1k_2[RH][I]}{k_{-1}+k_2[RH]} = -K[I] \qquad (5)$$

As to the relation between the rate of hydrogen abstraction and the structure of a substrate, we usually found the following order; *t*-C–H>*s*-C–H>*p*-C–H, as it was expected. However, the differences among them are rather small in this reaction. For example, the relative rates of hydrogen abstraction from different types of alkylbenzenes are, respectively: toluene (1.00 standard), ethylbenzene (1.27), and cumene (2.33) at 20°C. The relative rate of hydrogen abstraction of the triplet state of benzophenone has been investigated by Walling and Gibian,[2] who also determined the relative

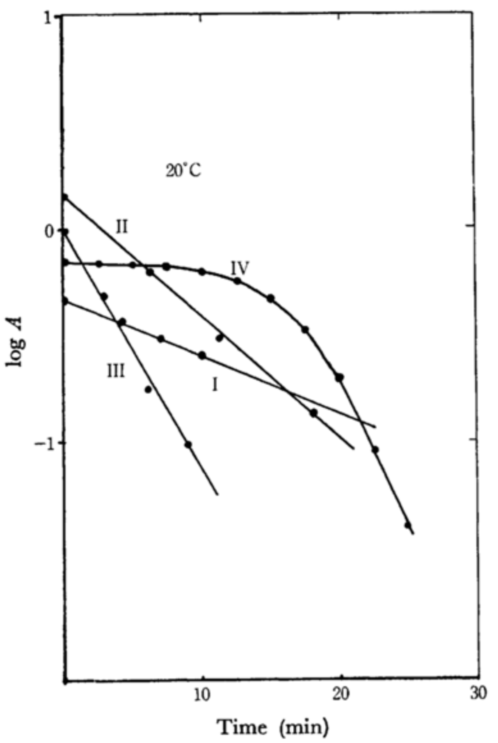


Fig. 1. I. methanol
II. ethanol
III. 2-propanol
IV. methanol in the presence of oxygen
(in this case sample was irradiated from the position of a half distance to light source through water layer for the sake of too slow decay to observe.)
A: Absorbance of phenanthraquinone

TABLE 2. RELATIVE REACTIVITY OF HYDROGENS OF HYDROCARBONS TOWARD VARIOUS RADICALS[a] (per hydrogen)

Type of C–H	$CH_3\cdot$ 182°C	$C_6H_5\cdot$ 60°C	*t*-BuO· 40°C	Cl· 23°C	$(C_6H_5)_2CO$ (T)[b] 22°C	PQ (T)[c]		F·[d] 23°C
						20°C	60°C	
Primary	1	1	1	1	1	1	1	1
Secondary	7	8—9.4	8—15	3.6	4.6	1.9	1.8	1.2
Tertiary	50	44	44	4.2	9.9	6.3	3.8	1.4

a) W. A. Pryor "Free Radicals," McGraw-Hill Book Co., New York (1966), p. 154.
b) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **86**, 3902 (1964).
c) This work. The values described in this table are not corrected for the abstraction of hydrogens on benzene ring and on *β*-carbon of side-chain, however, if corrected under the consideration of the values for benzene and *t*-butylbenzene, then the relative reactivity becomes;
1°:2°:3°=1:2.0:8.1 (20°C), 1:1.9:3.9 (60°C).
d) J. M. Tedder, *Quart. Rev.*, **14**, 339 (1960).

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[2] C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).

reactivity of C–H bonds to hydrogen abstraction. Such results are compared with others determined for several radicals in Table 2.

Since the relative selectivity to the different type of C–H bonds is a reflection of the reactivities of the radicals, we can conclude the high reactivity to hydrogen abstraction of the triplet state of phenanthraquinone (see Table 2). The reactivity is rather higher than that of benzophenone, and is roughly between that of the chlorine atom and that of the fluorine atom. Such a high reactivity is also indicated by the small temperature dependence of the relative rate and by the fact that benzene serves as a hydrogen donor.

Irregularities in the temperature dependence of the relative rate are observed in some substrates, especially 2-propanol and cumene.*1 The causes of these irregularity are not yet clear, but both the solvation and steric factors seem to be responsible. Concerning the photoreduced products of phenanthraquinone, a 1,2-addition compound of the VI type and a 1,4-addition compound of the VII type have been described in the literature.3) However, we can always find phenanthrahydroquinone and its quinhydrone as the main products, while the addition compounds form only a small portion.

Experimental

Materials and Irradiation. The phenanthraquinone was prepared by the oxidation of guaranteed-grade phenanthrene and was recrystallized from acetic acid three times (mp 207°C). With the exception of the alcohols, all the substrates used as solvents were dried over K-Na alloy and vacuum-sealed with a known amount of phenanthraquinone in an ordinary glass tube (8 mm in diameter, 50 mm long) by using the vacuum line. The alcohols were dried over calcium oxide. A sample was irradiated through water layer 400 mm thick and two ordinary glass layers 2 mm thick with 400-W high-pressure mercury arc lamp, while the decay of phenanthraquinone was followed spectrophotometrically at 420 mμ. The products were analysed by the TLC technique and were separated by means of a Florisil column.

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*1 These irregularities are not experimental errors, for they are reproducible.

3) M. B. Rubin, *J. Org. Chem.*, **28**, 1949 (1963); M. B. Rubin and P. Zwitkowits, *ibid.*, **29**, 2362 (1964); M. B. Rubin and R. G. LaBarge, *ibid.*, **31**, 3283 (1966); W. A. Waters, *J. Chem. Soc.*, **1953**, 3405; M. B. Rubin and Z. Neuwirth-Weiss, *Chem. Commun.*, **1968**, 1607.