

Preliminary Note

A photochemical application of kinetic electron spin resonance: Rates of hydrogen abstraction by triplet state carbonyl compounds

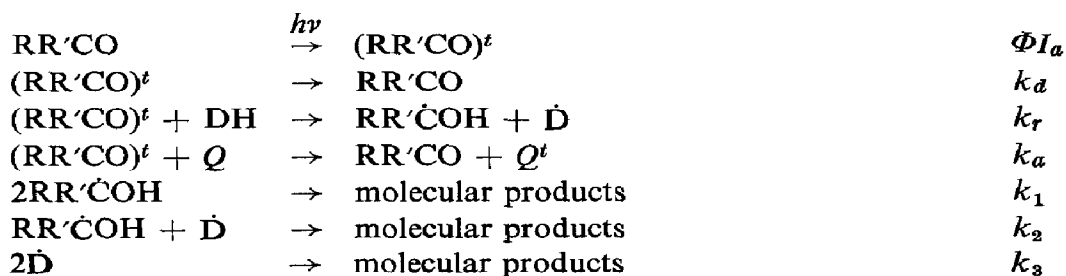
P. B. AYSCOUGH and R. C. SEALY

Department of Physical Chemistry, University of Leeds, Leeds LS2 9JT (Gt. Britain)

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Triplet state molecules are known to be intermediates in many photochemical reactions but relatively little is known about their reaction rates. Most of the data available at the moment are derived from measurements which rely on an assumed mechanism for the reaction. For instance, rate constants for the reactions of the n,π^* triplet state of several carbonyl compounds with suitable hydrogen donors have been determined by methods based on product analysis or flash photolysis¹. The initial products of such reactions are generally ketyl radicals, some of which have been characterized by electron spin resonance (ESR) methods. We have now developed the ESR-intermittent illumination technique used previously to measure termination rate constants of photolytically generated free radicals^{2,3} to enable us to estimate the rates of hydrogen abstraction by triplet-state molecules.

The following equations summarize the mechanism believed to hold for photoreduction of a carbonyl compound $RR'CO$ by a hydrogen donor DH in the presence of a triplet quencher Q :



A kinetic analysis yields the following expression for the ketyl radical concentration during continuous illumination:

$$[RR'\dot{C}OH]^{-2} = \frac{k_t}{\Phi I_a} \{1 + (k_a + k_q[Q])/k_r[DH]\}$$

$$\text{where } k_t = 2k_1 + k_2(k_1/k_3)^{1/2}.$$

Thus, a plot of $[\text{RR}'\dot{\text{C}}\text{OH}]^{-2}$ against $[Q]$ should be linear with the ratio gradient/intercept given by $[k_q/k_r[\text{DH}]]/[1 + (k_d/k_r[\text{DH}])]$. In the absence of an added quencher $[Q] = 0$ and from plots of $[\text{RR}'\dot{\text{C}}\text{OH}]^{-2}k_t^{-1}$ against $[\text{DH}]^{-1}$ the ratio gradient/intercept gives the value of k_d/k_r . Although k_r is dependent on solvent polarity⁴ its variation for the mixtures of organic solvents used can be ignored, and k_q , which depends on solvent viscosity, can be calculated according to the data of Wagner⁵. Therefore, the rate constant k_r for the hydrogen-abstraction reaction can be derived from measurements of the steady-state concentration of ketyl radicals $[\text{RR}'\dot{\text{C}}\text{OH}]$ in a given solvent with different amounts of added quencher and from measurements of $[\text{RR}'\dot{\text{C}}\text{OH}]$ and k_t in solvent mixtures using an inert solvent as diluent.

We have carried out such measurements for pyruvic acid in a variety of solvents using naphthalene as quencher and benzene as diluent. The filtered light from a 1 kW high pressure mercury lamp was employed²: the effective radiation was of 300–400 nm wavelength. In this region the absorption characteristics of pyruvic acid in the mixed solvents used did not vary significantly.

Figure 1 shows the experimental variation of $[\text{RR}'\dot{\text{C}}\text{OH}]_0^2/[\text{RR}'\dot{\text{C}}\text{OH}]^2$ (where $[\text{RR}'\dot{\text{C}}\text{OH}]_0$ is the steady state concentration in the absence of added quencher) with quencher concentration for two solvents under conditions in which essentially all the incident light was absorbed by the pyruvic acid.

Termination rate constants were determined as before² from the second-order decay of the ESR signals during the dark periods of intermittent illumination. From plots of $[\text{RR}'\dot{\text{C}}\text{OH}]^{-2}k_t^{-1}$ against $[\text{DH}]^{-1}$ experimental values of $k_d/k_r[\text{DH}]$ were less than 0.1 for the systems we examined, so that the ratios of gradient/intercept of the graphs shown in the figure are close to $k_q/k_r[\text{DH}]$ in each case.

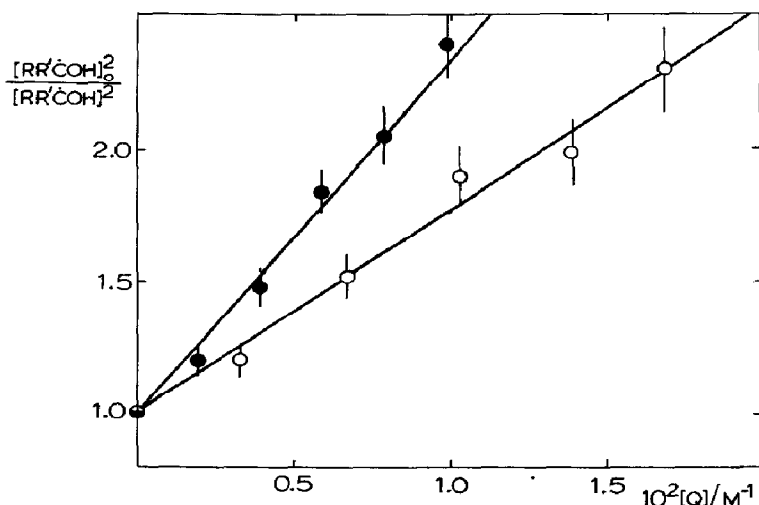


Fig. 1. Variation of steady state concentration of ketyl radicals with quencher concentration for pyruvic acid in ethanol and in 2-propanol, using naphthalene as quencher (Q): ●, ethanol; ○, 2-propanol.

Note that the kinetic scheme assumes that removal of the ketyl radical by reaction with quencher is negligible. This was demonstrated by measuring k_t (i) in the absence of quencher and (ii) at the highest quencher concentration employed, the rate constant being invariant within experimental error.

Abstraction rate constants for $^3(n,\pi^*)$ pyruvic acid from a series of hydrogen donors are given in Table I. Rate constants obtained by the kinetic-ESR method are seen to be in good agreement with those obtained from standard quenching studies⁶. Relative abstraction rates are seen to parallel those of simple alkoxy radicals⁷.

We have demonstrated the versatility of this kinetic-ESR technique by studying reactions of various triplet state ketones and quinones⁸. The main limitation is set by the rate of formation of the radicals: this limit is being further reduced in current investigations by improvements in the optical system.

TABLE I

| Solvent DH | $k_r/M^{-1}s^{-1}$ | | Relative rate per H atom |
|----------------------|--------------------|-------------------|-----------------------------|
| | Obs. | Lit. ⁶ | |
| t-Butanol | 2.2×10^6 | 2.3×10^6 | 0.02 |
| Methanol | 5.0×10^6 | | 0.15 |
| 2-Methyl propan-1-ol | 1.8×10^6 | | 0.82 |
| Ethanol | 2.3×10^6 | | 1.0 |
| 2-Butanol | 3.6×10^6 | | 3.3 |
| 2-Propanol | 4.1×10^6 | 5.2×10^6 | 3.7 |
| Benzyl alcohol | 1.4×10^7 | | 6.4 |
| 1-Phenyl alcohol | 1.8×10^7 | | 16 |

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