Concerning the Reactivity of Triplet 2-Pentanone

Sir:

It has been recently reported[1] that the extent of the Norrish type-II reaction from the excited singlet state of 2-pentanone depends on wavelength in the gas phase. Thus 35% of the type II originates from a singlet state at 3130 Å while 82% originates from this state at 2654 Å (as measured by the maximum quenching of the type II by diolefins). In solution similar quenching data yield a value of ≃12% for 3130-Å excitation[2] and lead to a rate constant for triplet reaction which differs by a factor of 3 from that reported for the gas phase. The gas-phase values were obtained by following the quenching of type-II products at low conversion (<1%), while the solution results are based on a quenching of the disappearance of the reactant ketone and were carried to high conversions (28 and 45% disappearance of reactant). The discrepancy between the two phases has prompted us to investigate the solution system by examining the quenching of the formation of type-II products at low conversions. Since processes other than the type II occur which lead to the disappearance of the parent ketone, and since a product of the type-II process, acetone, will absorb the incident light as effectively as 2-pentanone, it was felt that the discrepancy between the two phases might be resolved if the solution measurements were made at low conversions.

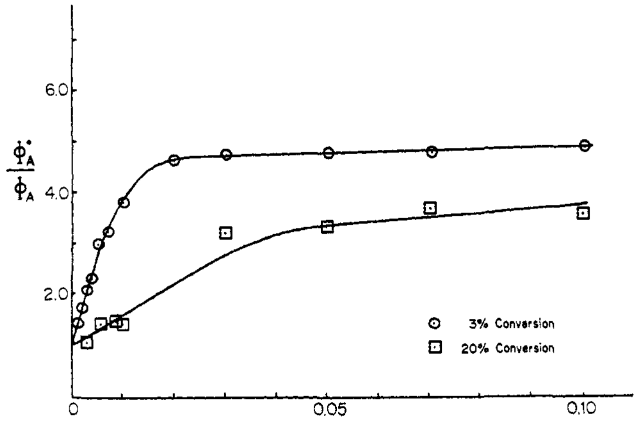

Figure 1. $\phi_A{}^0/\phi_A$ *vs.* [1,3-pentadiene]. The 3% conversion data are the average of three or four determinations at a given concentration. The 20% conversion data are from a single run (excitation in a Rayonet reactor; Rayonet 3100 lamps, Pyrex sample tubes).

Figure 1 shows the ratio of the quantum yield for acetone formation without 1,3-pentadiene to that with various concentrations of 1,3-pentadiene, $\phi_A{}^0/\phi_A$. Although not shown on Figure 1, the value of the quenching (85%) at 10 *M* pentadiene agrees well with that obtained by Wagner and Hammond,[2a] but the initial slope (380 l. mole^{-1}) is intermediate between their value (40 l. mole^{-1}) and that found in the gas phase[1] at 3130 Å (2020 l. mole^{-1}). The experiments were carried out to conversions of 3% or less (based on formation of acetone). In one experiment the conversion was extended to 20% and the slope of the resulting $\phi_A{}^0/\phi_A$ *vs.* (1,3-pentadiene) plot is about 60 l. mole^{-1} (*cf.* Figure 1). This slope is based on measurements of acetone production, and a similar plot of pentanone disappearance ratios yields a slope of 44 l. mole^{-1}. Thus the slope obtained in our high conversion experiments agrees with the work of Wagner and Hammond.

The slope at low conversions can be used to calculate the rate constant for triplet reactivity, k_r. An assumed value of the diffusion-controlled energy transfer rate constant,[3] $k_q = 2.45 \times 10^{10}$ l. mole^{-1} sec^{-1}, leads to $k_r = 6.4 \pm 0.2 \times 10^7$ sec^{-1} in agreement with the gas-phase value[1] of 6.4×10^7 sec^{-1}. Hence the rate constant for triplet reaction in the gas phase agrees with that in solution if the quenching rates are gas kinetic and diffusion controlled, respectively, and if the conversion is small. Perhaps differences in conversion also account for the irregular trend in initial slopes obtained for 2-hexanone,[2] 2-pentanone,[2] and 2-octanone.[4]

The extent of quenching in solution was also measured at 2537 Å using *cis*-3-methylpentene-2 as a triplet energy acceptor. In neat solutions of the pentene approximately 20% of the reaction was unquenched at both 3130 and 2537 Å, indicating that the gas-phase wavelength effect is eliminated in the solution phase. The rate of quenching was slower for the monolefin than for the diolefin at 3130 Å.

We have obtained preliminary results in heptane solutions for 2-hexanone (secondary γ-hydrogen) and 5-methyl-2-hexanone (tertiary γ-hydrogen) at low conversions. The approximate slopes of ϕ^0/ϕ *vs.* (1,3-pentadiene) plots for these ketones are 25 l. mole^{-1} and 4.0 l. mole^{-1}, respectively. These values can be compared with that of Wagner and Hammond for 2-hexanone[2] (10 l. mole^{-1}) at high conversion and that of Barltrop and Coyle for 5-methyl-2-hexanone[5] (5 l. mole^{-1}) at an unreported conversion.

There is current interest[6] in the nature of the triplet state (n–π* and/or π–π*) involved in the type-II reaction of aryl alkyl ketones. Comparison of the reactivity of the triplet state of the aryl alkyl ketones with alkyl ketones forms a basis for designating the nature of the triplet state of the former. Our results show that this comparison, to be valid, should be made with data obtained at low conversions.

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