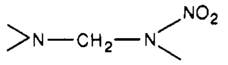
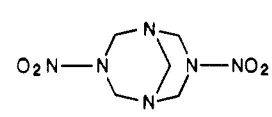
DATH is notable for the relatively low temperature and heating rate that are needed to induce the effect.

The essential features of the thermolysis of DATH can now be summarized. The thermal decomposition at 15 psi begins at about 15 K above the melting point and, according to the E_a values from TGA and DTA, is initiated by the azidomethyl groups. Both $N-N_2$ and $C-N_3$ bond homolyses are consistent processes. H atom abstraction leads to the formation of some HN_3 perhaps after $C-N_3$ bond fission occurs. A portion of this HN_3 is spewed to the gas phase where it is detected by IR spectroscopy. The radical residue of DATH proceeds to decompose via facile C–N bond fission steps which apparently have lower energy in this radical. The most stable products of this backbone depolymerization process, CH_2O and N_2O, escape to the gas phase. We know from our previous studies that N_2O and CH_2O are products common to most nitramines containing the fragment[1,4,10,22,23]



$$>N-CH_2-N<^{NO_2}$$

The facility of forming these products is especially great when the average N–N bond distances lies in the vicinity of 1.355–1.375 Å as it does in DATH, AZTC,[1] DPT,[4] and OHMX.[10] Some of the HN_3 that is formed probably fails to escape the condensed phase and remains to react with other fragments of the molecule to form a relatively more stable residue which decomposes above 500 K. It may not be coincidental that the compositionally related AZTC molecule thermally degrades in a very similar fashion. Recent studies have shown that analogous cyclic and acyclic nitramine pairs[10,23] decompose very similarly. It appears that this common behavior extends to cyclic and acyclic molecules in which the nitramine groups are joined by methyl azide groups.



DPT

Acknowledgment. We are grateful to D. O. Woolery (Rocketdyne) for providing a sample of DATH. This work was supported by the Air Force Office of Scientific Research, Aerospace Sciences, through Grant AFOSR-85-0356.

Registry No. DATH, 62209-57-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom coordinates (2 pages); tables of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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[23] Oyumi, Y.; Brill, T. B. *Combust. Flame*, in press.

Primary Processes in the Type I Photocleavage of Dibenzyl Ketones. A Pulsed Laser and Photochemically Induced Dynamic Nuclear Polarization Study

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The primary homolytic α-cleavage, and subsequent decarbonylation of the intermediate phenacyl radicals, have been studied for the type I photoreaction of a series of dibenzyl ketones, using the techniques of pulsed laser photolysis and photochemically induced dynamic nuclear polarization (photo-CIDNP). Evidence for selective primary cleavage to produce the most stable radical pairs is obtained for unsymmetrical ketones. The absolute rate constants and activation parameters for the decarbonylations are obtained, and the relationship between these and the stabilities of the product radicals is discussed.

Introduction

The most important features of the type I photocleavage of aromatic ketones can be described by the following equations for the example of an unsymmetrical dibenzyl ketone (Bz–CO–Bz′):

$$\text{Bz–CO–Bz}' \xrightarrow{h\nu} {}^1\text{Bz–CO–Bz}'^* \quad (1)$$

$${}^1\text{Bz–CO–Bz}'^* \rightarrow {}^3\text{Bz–CO–Bz}'^* \quad (2)$$

$${}^3\text{Bz–CO–Bz}'^* \rightarrow \text{Bz–CO}^\bullet + \text{Bz}^{\bullet\prime} \quad (3)$$

$$\text{Bz–CO}^\bullet + \text{Bz}^{\bullet\prime} \rightarrow \text{Bz–CO–Bz}' + \text{products} \quad (4)$$

$$\text{Bz–CO}^\bullet \rightarrow \text{Bz}^\bullet + \text{CO} \quad (5)$$

$$\text{Bz}^\bullet + \text{Bz}^{\bullet\prime} \rightarrow \text{products} \quad (6)$$

Homolytic α-cleavage occurs from the first excited triplet state of the ketone (3). The initially formed radicals either recombine to re-form the starting ketone, disproportionate to form products (4), or decarbonylation of the initially formed acyl radical occurs (5) followed by further combination or disproportionation reactions of the benzylic radicals to form other products (6).[1-3] The rate of the primary cleavage of the triplet state for dibenzyl ketone has been estimated to be ca. 10^{10} s^{-1} on the basis of trapping experiments.[1,2] Evidence for recombination of the primary radical products is available from photo-CIDNP investigations,[4] from photoracemization studies,[5] and from ^{13}C enrichment experiments.[6] Nevertheless the decarbonylation process is efficient and quantum yields for the reaction are often greater than 0.5.[5]

Although the qualitative aspects of the mechanism of the reaction are well understood, several quantitative aspects have yet to be established. For example, no direct measurement of the rate

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[†] Present address: Eastman Kodak Co., Rochester, NY 14650.

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[1] Engel, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 6074.

[2] Robbins, W. K.; Eastman, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6076, 6077.

[3] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummins: Menlo Park, 1978; Chapter 13.

[4] (a) Blank, B.; Mennitt, P. G.; Fischer, H. *Spec. Lect. Congr. Pure Appl. Chem. 23rd (1971)* **1971**, *4*, 1. (b) Fischer, H. *Pure Appl. Chem.* **1975**, *41*, 475.

[5] (a) Lewis, F. D.; Lauterbach, R. T.; Heine, H. G.; Hartmann, W.; Rudolph, H. *J. Am. Chem. Soc.* **1975**, *97*, 1519. (b) Lewis, F. D.; Magyar, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 5973.

[6] (a) Turro, N. J. *Pure Appl. Chem.* **1981**, *53*, 259 and references therein. (b) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 364 and references therein.

0022-3654/87/2091-0925$01.50/0

of the primary cleavage step (3) has been made, although evidence concerning the relative rates of cleavage of variously substituted ketones has been obtained by using CIDNP.[7] The rates of decarbonylation of several radicals have been determined,[8] although no systematic investigation of this process has been made.

In view of our interest in the type I reactions of dibenzyl ketones as probes of microheterogeneous environments,[6a] and of magnetic field and magnetic isotope effects,[6b] we have studied two aspects of these reactions using laser flash photolysis and photo-CIDNP techniques, namely the factors which control the preference for primary cleavage in unsymmetric ketones (3), and the rate of decarbonylation of the primary acyl radical (5). Previously pulsed laser techniques have been used by ourselves[9a] and Lunazzi, Ingold, and Scaiano[9b] in order to measure directly the decarbonylation rates of phenacyl radicals.

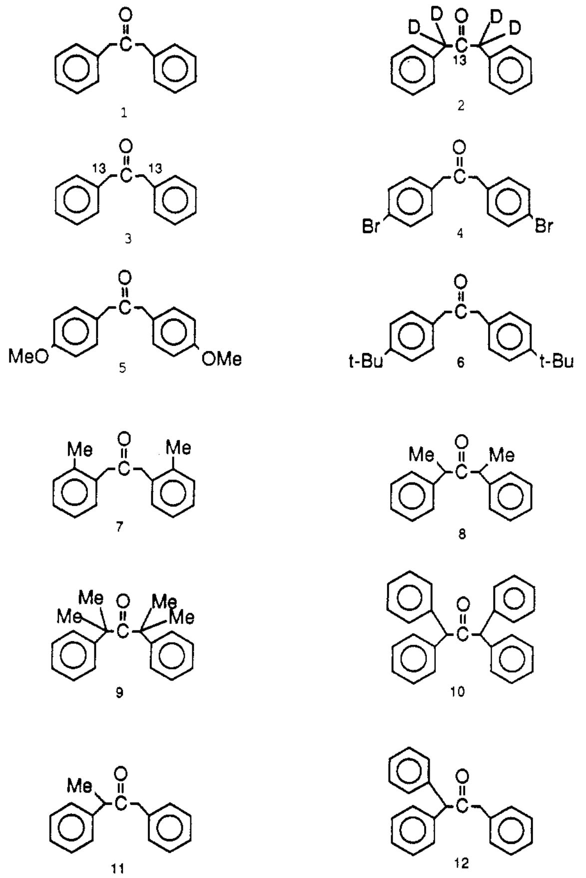
Experimental Section

Laser photolysis experiments were performed using a Lambda Physik excimer laser at 248 or 308 nm (EMG 101, 15 ns, ca. 50 mJ). The laser power was attenuated by using solution filters of varying optical density at the excitation wavelength. The experiments were performed using argon-purged solutions which were photolyzed in square Suprasil cells (8 mm × 8 mm) which were either equipped with arms for purging, or were incorporated into a flow system which allowed the contents of the cell to be changed without the solution coming into contact with air, or disturbing the position of the cell holder. Transient absorption was monitored at right angles to the excitation beam with a pulsed 450-W xenon arc lamp as the analyzing source. The transmitted light intensity was passed through an ISA H-10 monochromator and detected with an RCA 4840 photomultiplier tube. The output from the photomultiplier was terminated into 50 Ω and digitized by using a Tektronix 7912AD transient digitizer. The data were analyzed by using a PDP 11/23 minicomputer. The time-resolved growth signals were analyzed according to first-order kinetics. A typical fit to the data gave a standard deviation of ca. 5%; however, the errors derived from repeated measurements for any given sample were typically 10%. The variable-temperature experiments were performed with the sample cell rigidly held inside a quartz Dewar. The temperature was varied by purging the Dewar with nitrogen gas, which had been cooled by passage through copper coils immersed in liquid nitrogen and could be reheated by using a Nichrome wire heater. Using this technique the temperature of the sample could be varied from ca. 180 to 360 K, and stabilized to within 1 °C. The temperature was controlled by regulating both the nitrogen flow rate and the extent of reheating with the heater. The temperature of the samples was measured by using a copper–constantan thermocouple which was in intimate contact with the cell. The temperature could be measured to an accuracy of 0.5 °C. In a typical variable-temperature experiment the temperature was varied over a range of at least 50 °C, which generally corresponded to a change in the observed decarbonylation rate by a factor of 10.

CIDNP spectra were recorded on a Bruker WP-80 FT spectrometer as described previously.[10] Photolysis was performed by using a 1000-W xenon arc lamp which was filtered through an 8-cm aqueous solution of $NiSO_4$ which served as a heat filter, and transmitted light from 250 to 360 nm. The probe temperature was 305 K for all experiments.

Dibenzyl ketone (**1**) (Aldrich) was purified by crystallization from ether at low temperature. The isotopically substituted dibenzyl ketones (**2**, **3**), *p*,*p*′-dibromodibenzyl ketone (**4**), *p*,*p*′-dimethoxydibenzyl ketone (**5**), and *p*,*p*′-di-*tert*-butyldibenzyl ketone (**6**) were available from previous studies,[11,12] as were α,α′-dimethyldibenzyl ketone (**8**), α,α,α′,α′-tetramethyldibenzyl ketone (**9**), and tetraphenylpropanone (**10**).[13] *o*,*o*′-Dimethylbenzyl ketone (**7**), 1,3-diphenylbutan-2-one (**11**), and 1,3,4-triphenylpropan-2-one (**12**) were prepared as described elsewhere[14] (Scheme I). MBH spectrograde isooctane was used without further purification. All samples were deoxygenated by argon purging prior to use.

SCHEME I: Structures of the Compounds Used in the Present Study



Results

1. Laser Flash Photolysis of Dibenzyl Ketones. Laser flash photolysis of dibenzyl ketone (**1**) in isooctane solution leads to formation of a transient absorption monitored at 318 nm which appears within the laser pulse. After the laser pulse an additional growth in absorption is observed as a function of time, followed by a decay. The transient absorption spectrum which is observed at the time of maximum absorption is identical with that observed after the laser pulse, which is the same as the reported spectrum of the benzyl radical.[15] The initial absorption is assigned to the benzyl radical formed as a result of the primary cleavage reaction (3), and the growth in absorption is assigned to the decarbonylation step (5).

The rate of the growth in absorption is critically dependent upon the laser excitation energy. The benzyl radical products react by coupling reactions with a rate constant close to diffusion control.[16] This is a second-order process and thus the rate depends upon the concentration of the radical species present. Thus at higher laser energies more radicals are formed and the rate of radical decay

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[7] Johnston, L. J.; deMayo, P.; Wong, S. K. *J. Am. Chem. Soc.* **1982**, *104*, 307.

[8] (a) Solly, R. K.; Benson, S. W. *J. Am. Chem. Soc.* **1973**, *93*, 2127. (b) O'Neal, E.; Benson, S. W. *J. Chem. Phys.* **1962**, *36*, 2196. (c) Frey, H. M.; Vinall, I. C. *Int. J. Chem. Kinet.* **1973**, *5*, 523. (d) Watkins, K. W.; Thomson, W. W. *Int. J. Chem. Kinet.* **1973**, *5*, 791. (e) Kerr, J. A.; Lloyd, A. C. *Trans. Faraday Soc.* **1967**, *63*, 2480. (f) Schuh, J.; Hamilton, E. J.; Paul, H.; Fischer, H. *Helv. Chim. Acta.* **1974**, *57*, 2011.

[9] (a) Turro, N. J.; Gould, I. R.; Baretz, B. H. *J. Phys. Chem.* **1983**, *87*, 531. (b) Lunazzi, L.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1983**, *87*, 529.

[10] Lehr, G. F.; Turro, N. J. *Tetrahdron* **1981**, *37*, 3411.

[11] Turro, N. J.; Weed, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 1861.

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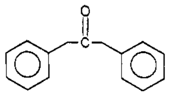
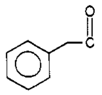
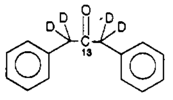
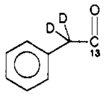
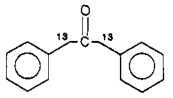
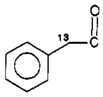
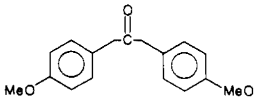
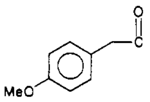
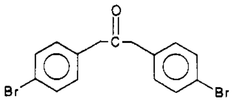
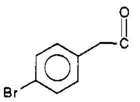
[13] Gould, I. R.; Zimmt, M. B.; Turro, N. J.; Baretz, B. H.; Lehr, G. F. *J. Am. Chem. Soc.* **1985**, *107*, 4607.

[14] (a) Baretz, B. H. Ph.D. Dissertation, Columbia University, 1983. (b) Turro, N. J.; Lei, X., results to be published.

[15] Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1958**, *34*, 1595.

[16] Claridge, R. F.; Fischer, H. *J. Phys. Chem.* **1983**, *87*, 1960.

TABLE I: Rate Constants for Decarbonylation of Phenacetyl Radicals at Room Temperature

ketone	radical	k_{-CO},[a] s^{-1}
		6.4×10^6
		6.1×10^6
		5.7×10^6
		1.5×10^7
		7.2×10^6

[a] The average errors determined from two standard deviations from typically four–six measurements are 15%.

competes with the rate of benzyl radical formation by decarbonylation. At lower laser energies the rate of the second-order dimerization is sufficiently slow that the growth in absorption due to decarbonylation is unaffected by the dimerization reactions. In practice the growth rate was monitored as a function of decreasing laser energy, which was controlled by using solution filters, until a constant value was obtained. Most of the experiments described in the present work were performed using a laser dose of ca. 5 mJ/cm^2.

Of the total maximum radical absorption signal, approximately 60% is formed within the pulse and 40% is due to the growth. It was expected that the ratio of immediately formed absorption to growth absorption would be 1:1 since one radical is formed in each case. The reason for the smaller than expected growth is not known but could be due to some photoinduced decarbonylation of the primary acetyl radicals formed within the laser pulse, or some absorption at the analyzing wavelength (318 nm) due to the acetyl radical,[17] although this latter explanation is less likely since the time-resolved absorption signals did not depend upon the analyzing wavelength over the narrow range of absorption of the benzyl radical (300–320 nm). In either case the growth kinetics will not be affected. The growth rate which is observed at room temperature is 6.4×10^6 s^{-1} for dibenzyl ketone. Similar experiments on the isotopically substituted ketones (**2**) and (**3**) result in values of 6.1×10^6 and 5.7×10^6 s^{-1} respectively (Table I).

Laser flash photolysis of the ortho- and para-substituted ketones **4**–**7** yields transient absorptions which are assignable to the corresponding benzyl radicals in each case.[15,16] The growth part of the signal for each ketone gives the decarbonylation rate constants for the corresponding substituted benzyl radicals as shown in Tables I and II.

Analysis of the radical growth rate for dibenzyl ketone as a function of temperature allows the determination of the Arrhenius parameters for the decarbonylation of the phenacetyl radical (typical data for the decarbonylation of the α-methylphenacetyl radical are shown in Figure 1) shown in Table II, together with the corresponding values for the *p-tert*-butylphenacetyl and *o*-methylphenacetyl radicals.

2. Flash Photolysis of Other Benzylic Radical Precursors. Flash photolysis of the α-substituted ketones **8**–**10** yields transient absorptions assignable to *sec*-phenethyl, cumyl, and diphenylmethyl radicals respectively.[15] For these ketones no time-resolved growth in absorption is observed at room temperature, but at lower temperatures this growth was observed in each case. The Arrhenius parameters for each of the decarbonylations are summarized in Table II.

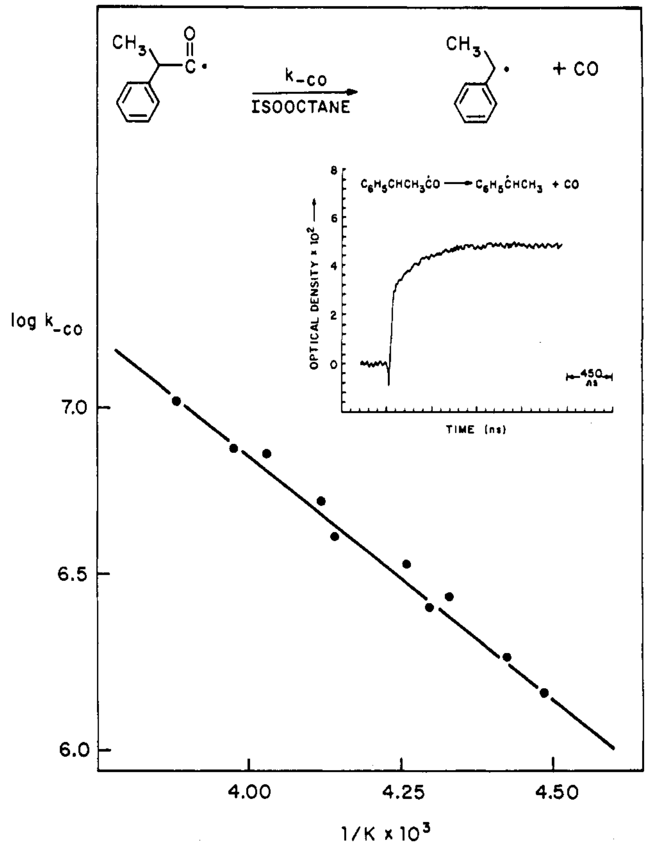


Figure 1. Arrenius plot for the decarbonylation of the α-methylphenacetyl radical formed upon pulsed laser photolysis of α,α′-dimethyldibenzyl ketone in argon-purged isooctane. Inset, time-resolved growth in absorption at 319 nm due to *sec*-phenethyl radicals following pulsed laser photolysis at 235 K.

3. Flash Photolysis of Unsymmetrical Ketones. Flash photolysis of the unsymmetrical ketones **11** and **12** also gave transients assignable to benzylic radicals. For ketone **11** decarbonylation was observed at 318 nm (the absorption maximum of the benzyl radical) at room temperature with a rate constant of 4.0×10^6 s^{-1}. Ketone **12** also showed growth in absorption at 318 nm with a rate of 6.0×10^6 s^{-1}, but no growth at 330 nm, which is the absorption maximum of the diphenylmethyl radical.

4. CIDNP Spectra of Unsubstituted Ketones. Photo-CIDNP of ketones **11** and **12** in benzene-d_6 was investigated. As observed previously in related studies on similar ketones,[4,7,18] polarization is observed in the starting ketone and in the radical coupling and disproportionation products, with the expected emission/absorption patterns for a triplet geminate radical pair, i.e., the regenerated starting materials were observed in emission and the products observed in absorption. In the case of ketone **12**, polarizations are observed in the starting ketone and the products, although in this case the emissive polarization is only observed in the methane proton (ca. 3.9 ppm) and not in the methylene protons (3.5 ppm).

Discussion

1. Initial Cleavage. CIDNP experiments have provided evidence for the relative rates of the primary cleavage step (3) for variously para-substituted ketones.[7] We can now compare the effect of substitution at the position α to the radical center. The decarbonylation process which is observed in the flash photolysis

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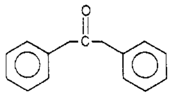
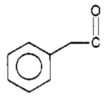
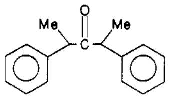
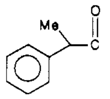
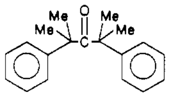
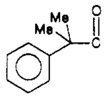
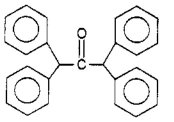
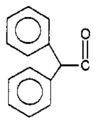
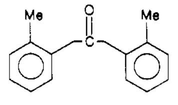
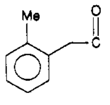
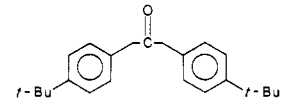
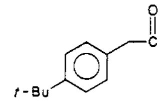
[17] (a) It has been reported that acyl radicals (e.g., the benzoyl radical, ref 17b) have absorptions in the 320-nm region, but we cannot estimate the extinction coefficient of the phenacyl radical at this wavelength from the literature data. (b) Schnabel, W. *J. Photogr. Eng.* **1979**, *23*, 154.

[18] Hutton, R. S.; Roth, H.; Kraeutler, B.; Cherry, W. R.; Turro, N. J. *J. Am. Chem. Soc.* **1979**, *101*, 2227.

TABLE II: Activation Parameters for Decarbonylation of Phenacetyl Radicals

ketone	radical	log A^a	E_a^a	k_{-CO} (300 K),^{b} s^{-1}
		11.0 ± 0.4	5.8 ± 0.5	6.4×10^6
		12.1 ± 0.7	6.0 ± 0.3	4.9×10^7
		11.1 ± 0.6	4.1 ± 0.5	1.5×10^8
		10.7 ± 0.4	3.4 ± 0.3	1.3×10^8
		11.8 ± 0.7	7.0 ± 0.3	4.5×10^6
		12.6 ± 0.4	7.5 ± 0.5	1.0×10^7

[a] Errors represent two standard deviations. [b] Calculated from activation parameters.

of the ketones **11** and **12** clearly suggests that the primary cleavage step in these ketones occurs to yield mainly the most substituted benzyl radical in each case (eq 7), since the rate of radical growth

$$^3PhCH_2COCRHPh^* \rightarrow PhCH_2CO^\bullet + {}^\bullet CRHPh \quad (7)$$
$$R = Me,Ph$$

is characteristic of decarbonylation of the phenacetyl radical. This same effect is observed in the photo-CIDNP spectra of these ketones. In each case the polarization observed in the benzylic methine of the starting ketone is greater than that observed in the methylene. We can assume that the extent of polarization is a direct measure of the number of radical recombinations which regenerate the starting ketone.[4,7] Thus the extent of polarization which is observed in a set of protons on the benzylic center adjacent to the carbonyl group is a measure of the number of primary cleavage events (3) which occured to yield a radical at that benzylic center. If primary cleavage in an unsymmetrical ketone occurs to yield one of the two possible benzyl radicals preferentially, then more polarization will be observed at that benzylic center in the regenerated ketone. For ketone **11** the ratio of the polarization observed in the two sets of benzylic protons is 7.5. This implies that α-methyl substitution increases the rate of cleavage in the triplet state of this ketone by a factor of 7.5 relative to the unsubstituted ketone, which is a large increase compared to the value of 1.5 observed for para substitution.[7] For ketone **12**, polarization is observed in the methine proton only. This implies that the effect of α-phenyl substitution is to increase the cleavage rate to the extent that only cleavage to yield the diphenylmethyl radical can be observed by using this technique. These substituent effects are almost certainly due to the increased stabilization in the product radicals.

2. Decarbonylation. The decarbonylation rates observed for the isotopically substituted ketones are within experimental error identical with that observed for the parent ketone (Table I). This result is not surprising since a mass isotope effect on the decarbonylation rate would not be expected. However, these results are important since magnetic isotope effects have been observed previously for photolysis of these ketones in micellar media.[6] The results support previous conclusions that the observed magnetic effects in micelles are due to the influence of the magnetic properties of the nuclei involved,[6] and not due to simple mass effects upon the decarbonylation process.

Some small differences in decarbonylation rates are observed (Table I) for the ring-substituted ketones **1**–**7**. In general a small increase in rate is observed for each of the ketones. This increase could be rationalized by assuming that the reaction rate is related to the stability of the product radicals since it has been suggested that both electron-donating and -withdrawing substituents stabilize radicals.[19] However, the current data is too limited to draw any definite conclusions concerning the effect of para substitution on the decarbonylation mechanism.

The activation energies and preexponential factors for the decarbonylations of several acyl radicals are summarized in Table II. The present results are in good agreement with those of the only other directly determined solution phase decarbonylation which has been reported, i.e., the pivoyl radical[8f] (E_a = 9.3 kcal mol^{-1}, log A = 11.9 in methylcyclohexane). The rate of decarbonylation of the radical **8a** is a factor of 7.5 greater than that of the radical **1a** (eq 8). This is the same as the difference in

$$PhCHRCO^\bullet \rightarrow PhCHR^\bullet + CO \quad (8)$$
$$\mathbf{1a},\ R = H$$
$$\mathbf{8a},\ R = Me$$

the relative rates of formation of the same benzylic product radicals from the primary cleavage of the triplet state of ketone **11**. Thus it appears that energetically it does not matter whether these radicals are formed by loss of CO or by cleavage of the triplet state and it is possible that the relative stabilities of the product radicals control the rates of both of these processes, although the current data are not sufficient to conclusively test this.[20]

Clearly there is a relationship between the product radical stability and the activation energy since substitution at the benzylic center tends to lower the activation energy, and the activation energy for the pivaloyl radical is the largest of all. However, some inconsistencies in the data are worth noting. For example, the α-methyl and o-methylphenacetyl radicals both have higher than expected activation energies, and lower than expected activation entropies. The differences are small and almost within the experimental error for each radical. Although we have no convincing explanation for these observations, the following points may be

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relevant. The preexponential factors for each radical are small which of course indicates a significant reduction in the degrees of freedom in the transmission state. In the present case this loss of freedom almost certainly arises because of a requirement that the ring π orbitals and the developing p orbital on the benzylic carbon align so as to allow the greatest stabilization of the product radical. This requirement will tend to "freeze" the rotation of the bond to the benzene ring. It is possible that this symmetrical conformation is disfavored in the unsymmetrical radicals from **7** and **8** and that a higher than expected activation energy might result.

Conclusion

From CIDNP and laser flash photolysis studies, the extent of preferential type I photocleavage for unsymmetrical dibenzyl ketones has been determined. In addition, using laser flash photolysis, the absolute rates of decarbonylation of the intermediate acyl radicals have been determined. Almost certainly the main factor which controls each process is the stability of the product benzylic radicals, although the results of variable-temperature studies suggest that other more subtle effects may play some role in unsymmetrical radicals.

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Evidence for Rapid Chain Growth in the Fischer–Tropsch Synthesis over Iron and Cobalt Catalysts

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We have examined hydrocarbon chain growth in the Fischer–Tropsch reaction by following both the rate and position of incorporation of ^{13}C into the hydrocarbon products after an abrupt switch from ^{12}CO to ^{13}CO in the reactant gas. On two catalysts (cobalt supported on silica and precipitated iron combined with various promoters) we find that ^{13}C appears after the isotope switch at the same rate in all positions of all products examined. Under the assumption that chain growth is unidirectional, this finding shows that chain growth on these catalysts is very rapid in comparison to the rate of isotope displacement in the precursors to chain growth. In addition, only a small portion of the active carbon on the surface can be in the form of hydrocarbon chains. Under these conditions no detailed information about the mechanism of chain growth is obtainable.

I. Introduction

A large effort has been expended to understand the mechanism of Fischer–Tropsch synthesis.[1] Many ingeneous experiments have proven the plausibility of various pathways, but the difficulty in making in situ measurements of proposed intermediates has frustrated an unequivocal definition of the mechanisms. Keys to understanding the mechanism are the surface concentrations and identities of active intermediates during the reaction.

We have examined the Fischer–Tropsch reacton by following both the rate and position of incorporation of ^{13}C into the C_1–C_6 hydrocarbon products after an abrupt switch of ^{13}CO for ^{12}CO in the reactant gas. Such isotopic transients under reaction steady state provide a valuable tool for the in situ study of complex reacting systems and are a special class of transient kinetic experiments. Recently, this technique has been used by several workers to study the formation of CH_4 from CO–H_2.[2-8] The emerging picture from these studies is that a small amount of carbon on the surface of synthesis catalysts is committed to the production of hydrocarbons. Chain growth in the Fischer–Tropsch reaction has received some attention.[3,6-8] Biloen et al.[6] placed a low bound on C–C bond formation rates on Co, Ru, and Ni by measuring the appearance rate of a new carbon isotope in C_3 fragments. We have published a brief communication of a portion of the results herein which show that chain growth is very rapid on an iron catalyst.[7]

Prior to these studies, estimates of chain growth (made from site turnover frequencies[1a,9,10] and non-steady-state experiments[11-13]) were 2–3 orders of magnitude slower. By studying the isotopic transient in detail, including the position dependence of isotope incorporation within the molecules, we can extend our knowledge about the chain growth process in the Fischer–Tropsch reaction. We can measure or set limits on the rates of individual reaction steps and on the coverages of the catalyst surface by reactive intermediates. The experiment addresses the number and

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