Substituent Effects on Hydrogen Abstraction by Phenyl Ketone Triplets

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Abstract: Triplet lifetimes in deaerated cyclopentane have been measured for a variety of ring-substituted benzophenones, acetophenones, and α-α-α-trifluoroacetophenones. The ketones undergo photoreduction under these conditions to mixtures of products formed from cyclopentyl and hemipinacol radicals. That triplet lifetimes are determined by rates of hydrogen abstraction from solvent is indicated by lifetimes being three times longer in cyclohexane-d_{12} than in cyclohexane-h_{12}. For the benzophenones, reciprocal lifetimes correlate comparably well with Hammett σ or σ^+ constants, with ρ values of 0.55 and 0.43, respectively. The effect of two substituents is best fitted to the sum of both σ values. These weak inductive effects are in accord with expectations for a reactive n,π* triplet. Rates for the acetophenones show the same substituent effects as previously observed for valerophenones; conjugating and electron-donating substituents stabilize the π,π* triplet and sharply reduce reactivity. Substituent effects are largest for the trifluoroacetophenones, consistent with their all having π,π* lowest triplets and reacting from weakly populated but highly reactive ($k > 10^7$ M^{-1} s^{-1}) n,π* states. Fluorine substitution, both on the ring and at the α-carbon, produces large rate enhancements, decafluorobenzophenone triplet being too short-lived to measure.

Although photoreduction of ketones in general and of benzophenone in particular is one of the best studied photoreactions, there has been no extensive study reported of how ring substituents on phenyl ketones affect rate constants for hydrogen atom abstraction. Ketone n,π* triplets are known to behave much like alkoxy radicals in their reactions.[1-3] The absence of systematic knowledge of how substituents affect rates of pure hydrogen atom abstraction by n,π* triplets has impeded understanding of systems which react by more complicated mechanisms. For example, ring substitution affects the electronic configuration of the lowest triplet, thus complicating interpretation of reactivity.[4,5] Another problem is that electron-deficient ketone triplets react with even weak donors such as alkylbenzenes by charge-transfer mechanisms which obscure the contribution of pure hydrogen atom abstraction.[6,7] We decided to circumvent these problems by measuring triplet lifetimes in cycloalkane solvents. We presume that triplet ketones can react with alkanes only by hydrogen atom abstraction. Therefore we first studied some photoreductions in cyclopentane to establish that the expected radical chemistry occurs. We then used pulsed laser kinetics techniques to measure the triplet lifetimes of a large number of substituted phenyl ketones. The results provide the first complete picture of how ring substituents affect n,π* triplet reactivity in ketones which have either n,π* or π,π* lowest triplets.

Results

Steady-State Studies. A degassed cyclopentane solution containing 0.1 M α-trifluoroacetophenone (TFA) was irradiated at 313 nm to 3% conversion. The following products were found, with the quantum yields listed in parentheses: cyclopentene (0.12); TFA-pinacol (0.10); 1-cyclopentyl-2,2,2-trifluoro-1-phenylethanol (0.08); 1-phenyl-2,2,2-trifluoroethanol (0.022); bicyclopentyl (0.021). These quantum efficiencies are conversion dependent, being only $^2/_3$ as large at 18% conversion. Product ratios remain the same to at least 30% conversion.

Degassed carbon tetrachloride solutions containing 0.1 to 1 M cyclopentane and 0.05 M of each of several substituted phenyl ketones were irradiated at 313 nm. In all cases, chlorocyclopentane was the major product, as anticipated from early studies.[1] Its formation was efficiently quenched by added naphthalene or 2,5-dimethyl-2,4-hexadiene. Maximum quantum yields (extrapolated to infinite cyclopentane) were 0.45, 0.26, and 0.25 for acetophenone (AP), benzophenone (BP), and TFA, respectively. Stern–Volmer quenching studies often gave nonlinear plots or different plots for different products. Analysis of the products

Table I. Selectivity of Triplet-State Hydrogen Abstraction from 2,3-Dimethylbutane by Substituted Benzophenones[a]

substitution	tert./prim.[b]	% C_2Cl_6[c]
4,4'-(MeO)$_2$	30	
4,4'-Me$_2$	39	50
none	75	68
4,4'-Cl$_2$	108	
4,4'-F$_2$	117	
4-CN	230	68

[a] 0.1 M ketone; 1.4 M dimethylbutane in CCl$_4$. [b] 2-Chloro-2,3-dimethylbutane/1-chloro-2,3-dimethylbutane. [c] 2[C$_2$Cl$_6$]/[C$_6$H$_{13}$Cl].

formed from TFA revealed a 9:1 ratio of chlorocyclopentane: PhC(OH)(CF$_3$)c-C$_5$H$_9$ for conversions ranging from 20 to 81%. The ratio of cyclopentane-containing products to ketone reacted was 1.6 ± 0.2. Chloroform was also formed; the ratio of CHCl$_3$ to chlorocyclopentane was 0.17 at 15% conversion. With benzophenone the latter ratio was 0.29 while that for chlorocyclopentane to carbinol was 38:1. The quantum yield for disappearance of benzophenone was quite low (<0.1) but was not measured precisely.

Several substituted benzophenones were irradiated in CCl$_4$-containing 1.4 M 2,3-dimethylbutane. Table I lists the ratios of 2-chloro/1-chloro products plus the relative amounts of hexachloroethane formed.

Laser Flash Studies. A large number of ring-substituted acetophenones, benzophenones, and α-trifluoroacetophenones were studied by the same general procedure. Enough ketone was dissolved in cyclopentane to give optical densities near 0.6 at 337 nm or 0.2 at 308 nm. The concentrations involved range from 0.005 to 0.02 M. The solutions were deaerated by bubbling purified nitrogen through them for several minutes. They were then excited with either a nitrogen laser ($\sim$10 mJ/6-ns pulse at 337 nm) or an excimer laser ($\sim$80 mJ/4-ns pulse at 308 nm),

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†NRCC Contribution No. 24677.

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(2) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.
(3) Griller, D.; Howard, J. A.; Marriott, P. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619.
(4) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604 and references therein.
(5) (a) Porter, G.; Suppan, P. *Trans. Faraday Soc.* **1965**, *61*, 1664. (b) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbery, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466. (c) Berger, M.; McAlpine, E.; Steel, C. *Ibid* **1978**, *100*, 5147.
(6) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040.
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Table II. Substituent Effects on Decay Rates of Triplet Benzophenone in Deaerated Cyclopentane at Room Temperature

substituent	σ^a	$1/\tau^b$, 10^6 s^{-1}	$(1/\tau)_{corr}{}^c$, 10^6 s^{-1}
4,4'-(MeO)$_2$	-0.54	1.9	1.4
4-MeO	-0.27	3.4	2.9
4,4'-(t-Bu)$_2$	-0.40	3.2	2.7
4,4'-(Me)$_2$	-0.34	3.5	3.0
4-Me	-0.17	4.5	4.0
3,3'-(Me)$_2$	-0.14	3.7	3.2
3-Me	-0.07	4.7	4.2
H	0	5.3	4.8
4-F	0.06	6.5	6.0
4,4'-(F)$_2$	0.12	8.3	7.8
4-Cl	0.23	6.3	5.8
3-Cl	0.37	7.65	7.2
4-MeO-4'-CN	0.39	4.7	4.5
4-CO$_2$Me	0.39	7.6	7.1
4,4'-(Cl)$_2$	0.46	8.6	8.1
3,4-(Cl)$_2$	0.60	9.3	8.8
3-CF$_3$	0.43	10.8	10.3
4-CF$_3$	0.54	10.3	9.8
3-CN	0.56	13.0	12.5
4-CN	0.66	11.0	10.5
4,4'-(CN)$_2$	1.32	23.7	23.2
2-CO$_2$Me		9.5	9.0
F$_5$		49.6	49.1
F$_{10}$		>140	>140

^{a}Reference 16. ^{b}Actual measurements. ^{c}0.5 $\times$ 10^6 Subtracted.

Table III. Substituent Effects on Decay Rates of Triplet Acetophenone in Deaerated Cyclopentane at Room Temperature

substituent	$1/\tau$, 10^6 s^{-1}	substituent	$1/\tau$, 10^6 s^{-1}
4-MeO	0.58	4-CN	3.8
3-MeO	0.85	H	5.3
4-COCH$_3$	1.0	3-Cl	7.7
4-t-Bu	1.4	3-CF$_3$	15.0
4-Me	1.75	4-CF$_3$	11.9
4-Cl	2.2		

Table IV. Substituent Effects on Decay Rates of Triplet α-Trifluoroacetophenone in Deaerated Cyclopentane at Room Temperature

substituent	$1/\tau$, 10^6 s^{-1}	substituent	$1/\tau$, 10^6 s^{-1}
4-MeO	0.60	3-Cl	10.2
3,4-Me$_2$	0.98	H	13.6
4-COCH$_3$	1.5	4-F	18.6
4-t-Bu	2.7	4-CF$_3$	98
3-Me	5.3	3-CF$_3$	150
4-Cl	3.6		

and their triplet decay was measured. The apparatus has been described previously.[8] Triplet decay was measured between 525 and 600 nm for the benzophenones, 365 and 440 nm for the acetophenones, and 375 and 425 nm for the trifluoroacetophenones. The exact wavelength was chosen to minimize the amount of residual transient absorption due to hemipinacol radicals. There was no doubt that the transients studied were triplets, based on their absorption spectra, lifetimes, and ability to be quenched by dienes. In a few cases hemipinacol radical decay was monitored at long delays and found to be second order, as expected. In every case examined, triplet decay rates were cleanly exponential and were independent of both excitation and monitoring wavelengths. The longest lifetimes obtainable were 2000 ns and are determined presumably by solvent impurity and residual oxygen quenching.

Table II lists all the decay rates measured for substituted benzophenones, and Tables III and IV contain the measurements for the acetophenones and trifluoroacetophenones. Reproducibility averaged better than ±3% for a given bottle of cyclopentane. Most of the values in the tables were obtained for one bottle of solvent. The few that were not have been adjusted for the small variation

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Table V. Triplet Lifetimes (in ns) in Cyclohexane and Cyclohexane-d_{12}

ketone	C$_6$H$_{12}$	C$_6$D$_{12}$
PhCOPh	156	430
PhCOCH$_3$		516
PhCOCF$_3$	55	163

Scheme I
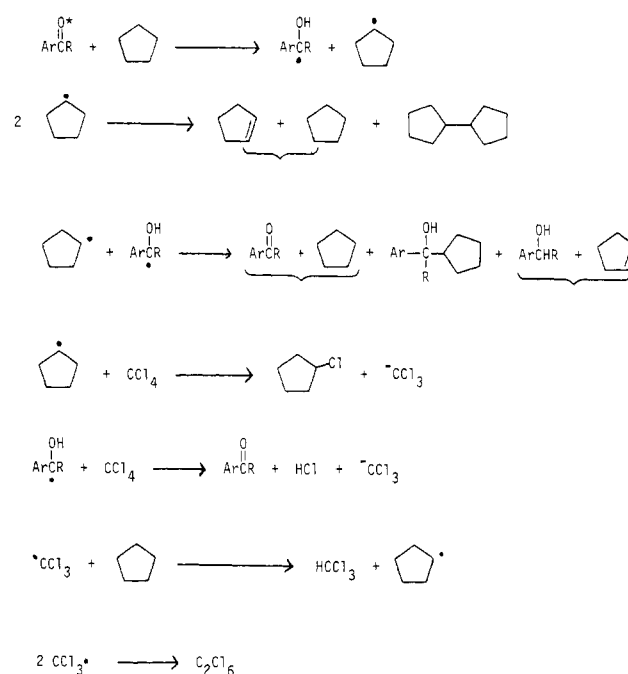
(±10%) in the lifetime of unsubstituted benzophenone.

A few special experiments were run. One experiment was conducted with p-F-TFA in carbon tetrachloride containing 1 M cyclopentane. The decay rate measured was 2.9 $\times$ 10^6 s^{-1}. That in CCl$_4$ containing no cyclopentane was 0.5 $\times$ 10^6 s^{-1}. The difference, 2.4 $\times$ 10^6 s^{-1}, represents the quenching due to the 1 M cyclopentane. Finally, the triplet decay rates of BP, AP, and TFA were measured in cyclohexane and cyclohexane-d_{12}. Table V lists the isotope effects observed.

Discussion

Several pieces of evidence indicate that the predominant reaction of triplet ketones in cyclopentane solvent is hydrogen abstraction to generate cyclopentyl and hydroxybenzyl radicals. All the products expected from coupling and disproportionation of these radicals are indeed observed in a quantum yield of 0.2 with TFA. Quantum yields well below unity are common in ketone photoreductions because of efficient disproportionation of primary radicals back to ground-state reactants.[7] Similar observations have been made for other ketones in cyclohexane.[9]

In CCl$_4$ a short-chain reaction involving CCl$_3$ radicals produces some cyclopentyl chloride, but the low yields of chloroform and high yields of hexachloroethane (with dimethylbutane) indicate that the majority comes from efficient solvent scavenging of cyclopentyl radicals produced by triplet ketone. Walling and Gibian reached the same conclusion, although they detected no chloroform.[1] With benzophenone, most of the hemipinacol radicals appear to be oxidized to ketone, as CCl$_4$ is known to do,[10] since quantum yields of ketone disappearance are low. The less oxidizable TFA gives better yields of products derived from hemipinacol radicals. The competing chain reaction and the variable Stern–Volmer plots precluded obtention of relialbe kinetics parameters. These product studies merely reinforce the conclusion

(9) Wagner, P. J.; Thomas, M. J. *J. Chem. Soc.* **1979**, *101*, 4173.

(10) Willson, R. L.; Slater, T. F. In "Fast Processes in Radiation Chemistry and Biology"; Adam, G. E., Fielder, E. M. Michael, B. D., Eds.; Wiley: New York, 1975; p 153.

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Figure 1. Hamett plot for uncorrected triplet decay rates of ring-substituted benzophenones in cyclopentane vs. σ constants.

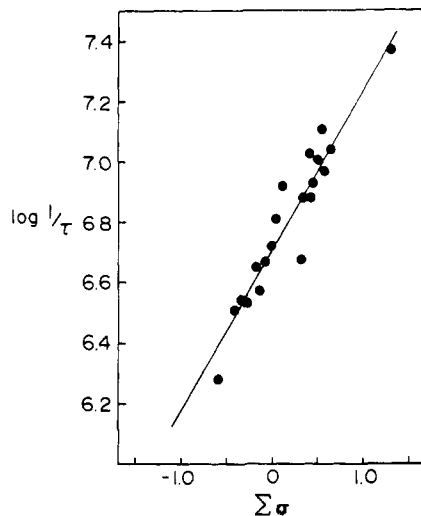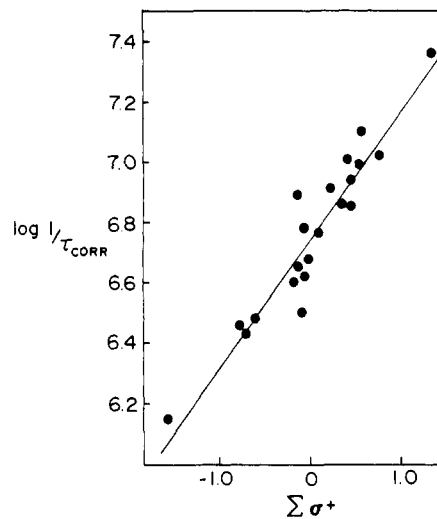**Figure 2.** Hammett plot for corrected triplet decay rates of ring-substituted benzophenones in cyclopentane vs. σ^+ constants.

Scheme II

of efficient hydrogen abstraction and provide necessary information for interpreting alkyl chloride product ratios in terms of relative rates of hydrogen abstraction.

For most of the ketones, triplet lifetimes are much shorter than the maximum value of 2000 ns observed for the unreactive methoxyacetophenones. Therefore quenching by impurities makes either minor or negligible contributions to the decay rates. Likewise, self-quenching by ground-state ketone would operate at actual pseudo-unimolecular rate constants no greater than 10^5 s^{-1} for the concentrations used.[11]

That triplet decay rates are determined almost exclusively by reaction with solvent is indicated by the significant isotope effects observed in cyclohexane-d_{12} relative to cyclohexane itself. Of course, the k_H/k_D value of 3 is a combination of primary and secondary effects; but it clearly establishes that hydrogen atom abstraction is the major mechanism for triplet decay in all three unsubstituted ketones. We conclude that such is also the case of all of the substituted ketones. Comparable isotope effects were reported for hydrogen abstraction by triplet benzophenone from 2-propanol[12] and from 1,4-cyclohexandiene,[13] while a value of 4.8 has been measured for γ-hydrogen abstraction in triplet nonanophenone.[14]

This work was not an attempt to measure absolute rate constants for hydrogen abstraction from cyclopentane. The simple objective was to provide a constant environment which would favor hydrogen atom abstraction to the greatest possible extent. Thus cyclopentane serves as both constant solvent and substrate of constant concentration. The one experiment conducted with 1 M cyclopentane in CCl_4 indicates that hydrogen abstraction is eight times more rapid in neat (10.6 M) cyclopentane. We conclude that the real bimolecular rate constants can be approximated quite closely by dividing the rates measured in cyclopentane by the concentration of solvent. Moreover, quenching by processes other than hydrogen abstraction appears to be so minimal that proper corrections to observed decay rates were not really necessary. Our decay rates compare well with literature reports for similar situations: $1/\tau = 3-4 \times 10^6$ s^{-1} for acetophenone[15a] and benzophenone[15b] in neat cyclohexane: k_H(cyclohexane) $= 4-7 \times 10^5$ M^{-1} s^{-1} in benzene or acetonitrile.[11c]
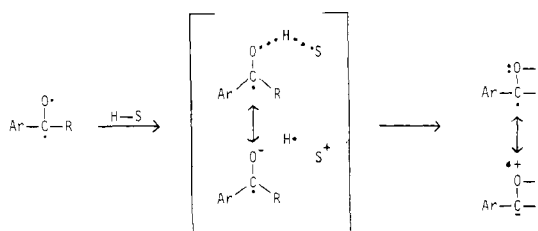
Benzophenones. All of the benzophenones included in this study are known to have n,π^* lowest triplets.[16] Therefore the relative decay rates in Table I provide an accurate measure of substituent effects on rates of hydrogen abstraction by n,π^* triplets. The total spread of reactivities encompasses just one order of magnitude. Figure 1 displays a plot of the log $(1/\tau)$ values plotted against the sum of regular Hammett σ constants.[17] The slope is $+0.55 \pm 0.03$ with a correlation coefficient of 0.97. Given the small variations in triplet lifetimes, the fit is excellent. If 5×10^5 s^{-1}, the rate of decay of the unreactive triplet p-methoxyacetophenone, is taken as the rate of impurity quenching and substracted from all decay rates, a slightly steeper Hammett plot results, with $\rho = 0.59 \pm 0.05$.

The quite small value of ρ and the fact that the effect of two substituents is so accurately reflected by the sum of their σ constants indicate that the substituents provide only weak inductive effects on hydrogen abstraction. The most dramatic example of the lack of any conjugative substituent effect is provided by the 4-methoxy-4'-cyano ketone, in which the two substituents almost exactly offset each other. No significant conjugative effect was really expected. The triplet has an electronic distribution much like that of a benzyl radical, as is evident in the similar absorption spectra of ketone triplets and their hemipinacol radicals.[18] Therefore there is little change in π-electron density, especially at the carbonyl carbon, in proceeding from triplet to radical.[19] Neither is there any large change in dipole during the hydrogen abstraction reaction. In constrast, Arnold and co-workers have shown clearly that substituent effects on triplet energies involve a superposition of conjugative stabilization of the free spin at the benzyl carbon and an inductive effect on the change in dipole

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(13) Encias, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

(14) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480.

(15) (a) Lutz, H.; Lindqvist, L. *Chem. Commun.* **1971**, 493. (b) Porter, G.; Topp, M. R. *Proc. R. Soc. London, A* **1970**, *315*, 163.

(16) Kearns and Case (Kearns D. R.; Case, W. A. *J. Am. Chem. Soc.* **1966**, *88*, 5087) showed that 4,4'-diemthoxybenzophenone has an n,π^* lowest triplet. All other subtituents have a smaller effect that methoxy.

(17) Kosower, E. M. "An Introduciton to Physical Organic Chemistry"; Wiley: New York, 1968; p 49.

(18) (a) Tsubomura, H.; Yamamoto, N.; Tanaka, S. *Chem. Phys. Lett.* **1967**, *1*, 309. (b) Lutz, H.; Breheret, E.; Lindqvist, L. *J. Phys. Chem.* **1973**, *77*, 1758.

(19) Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1667, 1672.

moment connected with electronic excitation.[20]   Thus there is no correlation observed or expected between triplet energies and rate constants, as long as hydrogen abstraction remains exothermic.

The positive ρ value indicates a small degree of charge transfer stabilization of the transition state for hydrogen abstraction (Scheme II),[21] as was apparent earlier in the effects of δ and more remote substituents on rates of γ-hydrogen abstraction by triplet phenyl ketones.[2,21b] Thus the ρ_I value of -1.85 displayed by δ-substituents indicates that the C–H center is the electron donor in the transition state. The current results demonstate the anticipated corollary, that the carbonyl is the electron acceptor.

As is usual with Hammett correlations, neither σ nor σ^+ constants predict the observed decay rates perfectly. In fact, a plot vs. σ^+ values (Figure 2) has a slope of 0.43 ± 0.03 with a correlation coefficient of 0.97. p-Methoxy substitution has a large enough deactivating effect that a correlation with a weighted mixture of σ and σ^+ constants probably would be appropriate. We chose not to attempt this feat since the behavior already discussed provides sufficiently useful mechanistic information: hydrogen abstraction behaves like a typical free radical reaction. Although the overall process is called photoreduction, and hydrogen atom transfer technically is a one-electron reduction, there is no net charge separation and the ρ value reflects only transition-state polarization.

The rate enhancement produced by fluoro substituents is much greater than that predicted by pure σ constants and in the opposite direction from that predicted by σ^+ constants. In fact, exclusion of the results for the fluoro ketones produces a much better correlation with σ^+. We shall consider these unusual reactivity enhancements separately, but note that the enhancement is so great that decafluorobenzophenone triplet is too reactive to measure exactly.

The results in Table I provide further evidence for a charge-separated transition state for hydrogen abstraction. The quantitative trapping of alkyl radicals by CCl_4 and the low reactivity of CCl_3 radicals combine to make simple product ratios such as in Table I good indicators of relative reactivities. There is a significant substituent effect on the ratio of tertiary/primary radicals formed from dimethylbutane. The direction of the substituent effect clearly indicates charge transfer from alkane to ketone, since the more easily reduced ketones produce more tertiary radicals, which of course are more easily oxidized than primary radicals. The product ratios in the table do not reflect relative rates of tertiary/primary radical production exactly because of the small amount of competing hydrogen abstraction by CCl_3 radicals. This problem should be most severe for the ketones with the most oxidizable hemipinacol radicals, which would react most efficiently with CCl_4. Since CCl_3 radical has a very high tertiary/primary selectivity,[22] the product ratios which we measured for p-methoxy- and p-methylbenzophenone are presumably somewhat *higher* than the values which would reflect pure triplet ketone hydrogen abstraction.

We did not look systematically at ortho-substituents. Since o-carbomethoxybenzophenone is even more reactive than the para-isomer, it seems that steric efects on reactivity are minimal, as opposed to the sizable effects of α-substitution.[23]

Acetophenones. Each of the acetophenones with n,π^* lowest triplets displays a decay rate very similar to that of the comparably substituted benzophenone. All electron-donating substituents ($\sigma < 0$) and all conjugating substituents cause π,π^* triplets to be lowest.[4,24] These ketones display rate constant reductions exactly parallel to those measured for γ-hydrogen abstraction by comparably substituted valerophenones.[4,24] The reactivity changes are depicted in Figure 3, where the line represents the benzophenone plot of Figure 1. These results reinforce the interpretation
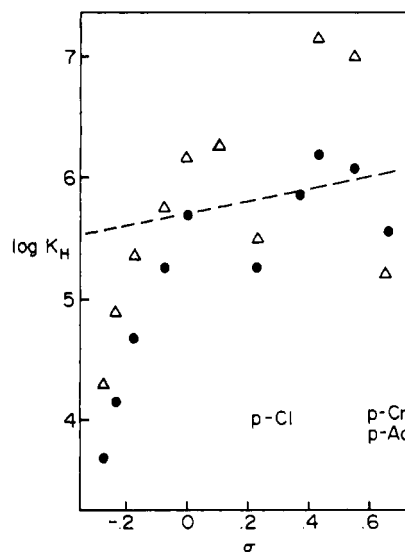

Figure 3. Rate constants for hydrogen abstraction from cyclopentane plotted against Hammett σ values: (●) substituted acetophenones and (△) substituted α-trifluoroacetophenones; dashed line is plot from Figure 1.

published earlier of Norrish type II reactivity, that all ketones react from equilibrium populations of n,π^* triplets, which are subject to the same small substituent effects now measured directly for the benzophenones.
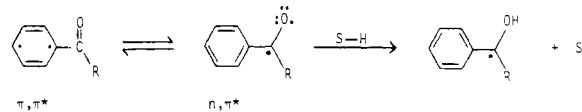
It is worth pointing out explicitly the nearly identical reactivities of triplet benzophenone and acetophenone. This fact is in line with the above reasoning regarding energetics and demonstrates the similar nature of the two ketones' n,π^* lowest triplet states.

Trifluoroacetophenones. We have interpreted all of our earlier results with α-trifluoroacetophenones in terms of their having π,π^* lowest triplets.[7,25] The current results, as presented in Figure 3, reinforce that viewpoint, inasmuch as reactivity in "pure" hydrogen abstraction measures the equilibrium population of n,π^* triplets.[4,5] All substituents which lower π,π^* relative to n,π^* energies (alkyl, acyl, alkoxy) decrease the equilibrium n,π^* concentration and therefore reduce the observed triplet reactivity toward cyclopentane. A p-F has no significant effect on energy levels[4] and produces the same inductive effect noted with benzophenones. CF_3 substituents produce high reactivities; the order of magnitude increases are much greater than the 2-fold inductive effects displayed when the parent ketone has an n,π^* lowest triplet. CF_3 substitution is expected to stabilize the n,π^* triplet of phenyl ketones relative to the π,π^* triplet.[4,25,26] Therefore we conclude that the two CF_3–TFA's have n,π^* and π,π^* triplets of comparable energies and population, since the plot in Figure 3 has not yet flattened to the extent that it does for acetophenones. The n,π^* population in triplet TFA itself is probably no more than 10% in nonpolar solvents.[7]

Summary

Ring substituents produce relatively small inductive effects on hydrogen atom abstraction by n,π^* ketone triplets, as would be expected for an electron-deficient radical species. The good Hammett correlation stands in marked contrast to processes which involve significant electron transfer, such as reaction with alkylbenzenes[7,25,27] or alkenes.[28]

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(21) (a) Russell, G. A. *J. Org. Chem.* **1958**, *23*, 1407. (b) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.
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(24) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329.

(25) Wagner, P. J.; Lam, H. M. H. *J. Am. Chem. Soc.* **1980**, *102*, 4167.
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(28) Caldwell, R. A.; Sovocool, G. W.; Gajewski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549.

Experimental Section

Chemicals. Ketones either were obtained from commerical sources and purified or were synthesized by well-established methods. A complete description will appear in a separate paper.[27] Both 4,4'-dicyanobenzophenone and 4-cyano-4'-methoxybenzophenone were obtained from Professor Donald Arnold. Two varieties of cyclopentane were used. All product studies were done with Mallinckrodt reagent grade which had been washed with sulfuric acid, neutralized, dried, and distilled. This material was shown by GC analysis to contain $<10^{-4}$ M cyclopentente; the only volatile impurities were traces of other saturated alkanes. The solvent used for most laser kinetics measurements was Aldrich Gold Label spectrophotometric grade cyclopentane, and it was used as received. Several kinetics runs were done with the carefully purified cyclopentane as well. Identical triplet lifetimes were obtained in both solvents for all ketones with lifetimes less than 150 ns. Longer lifetimes were obtained in the *unpurified* solvent for the longest lived triplets, and, therefore, the reported lifetimes are those measured in this solvent. We assume that a small amount of a triplet quencher was present in the "purified" material.

Product studies were conducted as usual[4] by gas chromatographic analysis of irradiated solutions. Product concentrations were determined by comparison to known concentrations ($\sim$0.003 M) of inert internal standards: dodecane and hexadecane for the products from cyclopentane; chlorobenzene for chlorocyclopentane. Actinometry was provided by parallel irradiation of valerophenone samples.[29]

Flash kinetics was conducted as described in the literature.[8] Samples were contained in 7 × 7 mm quartz cells fitted at the top with septa to allow nitrogen purging. Proper deaerating times were determined by measuring lifetimes until further purging produced no change.

Registry No. (CH$_3$)$_2$CHCH(CH$_3$)$_2$, 79-29-8; (4-MeOC$_6$H$_4$)$_2$CO, 90-96-0; (4-MeC$_6$H$_4$)$_2$CO, 611-97-2; (C$_6$H$_5$)$_2$CO, 119-61-9; (4-ClC$_6$H$_4$)$_2$CO, 90-98-2; (4-FC$_6$H$_4$)$_2$CO, 345-92-6; 4-NCC$_6$H$_4$COC$_6$H$_5$, 1503-49-7; PhCOCH$_3$, 98-86-2; PhCOCF$_3$, 434-45-7; 4-MeOC$_6$H$_4$COC$_6$H$_5$, 611-94-9; (4-*t*-BuC$_6$H$_4$)$_2$CO, 15796-82-4; (3-MeC$_6$H$_4$)$_2$CO, 2852-68-8; 3-MeC$_6$H$_4$COC$_6$H$_5$, 643-65-2; 4-FC$_6$H$_4$COC$_6$H$_5$, 345-83-5; (4-FC$_6$H$_4$)$_2$CO, 345-92-6; 4-ClC$_6$H$_4$COC$_6$H$_5$, 134-85-0; 3-ClC$_6$H$_4$COC$_6$H$_5$, 1016-78-0; 4-MeOC$_6$H$_4$COC$_6$H$_4$CN-4, 27645-60-9; 4-MeOCOC$_6$H$_4$COC$_6$H$_5$, 6158-54-9; (4-ClC$_6$H$_4$)$_2$CO, 90-98-2; 3,4(Cl)$_2$C$_6$H$_3$COC$_6$H$_5$, 6284-79-3; 3-F$_3$CC$_6$H$_4$COC$_6$H$_5$, 728-81-4; 4-F$_3$CC$_6$H$_4$COC$_6$H$_5$, 728-86-9; 3-NCC$_6$H$_4$COC$_6$H$_5$, 6136-62-5; (4-NCC$_6$H$_4$)$_2$CO, 32446-66-5; 2-MeOCOC$_6$H$_4$COC$_6$H$_5$, 606-28-0; C$_6$F$_5$COC$_6$H$_5$, 1536-23-8; (C$_6$F$_5$)$_2$CO, 853-39-4; 4-MeOC$_6$H$_4$COCH$_3$, 100-06-1; 3-MeOC$_6$H$_4$COCH$_3$, 586-37-8; 4-CH$_3$COC$_6$H$_4$COCH$_3$, 1009-61-6; 4-*t*-BuC$_6$H$_4$COCH$_3$, 943-27-1; 4-MeC$_6$H$_4$COCH$_3$, 122-00-9; 4-ClC$_6$H$_4$COCH$_3$, 99-91-2; 4-NCC$_6$H$_4$COCH$_3$, 1443-80-7; 3-ClC$_6$H$_4$COCH$_3$, 99-02-5; 3-F$_3$CC$_6$H$_4$COCH$_3$, 349-76-8; 4-F$_3$CC$_6$H$_4$COCH$_3$, 709-63-7; 4-MeOC$_6$H$_4$COCF$_3$, 711-38-6; 3,4-(Me)$_2$C$_6$H$_3$COCF$_3$, 75833-26-0; 4-CH$_3$COC$_6$H$_4$COCF$_3$, 86988-49-0; 4-*t*-BuC$_6$H$_4$COCF$_3$, 73471-97-3; 3-MeC$_6$H$_4$COCF$_3$, 1736-06-7; 4-ClC$_6$H$_4$COCF$_3$, 321-37-9; 3-ClC$_6$H$_4$COCF$_3$, 321-31-3; 4-FC$_6$H$_4$COCF$_3$, 655-32-3; 4-F$_3$CC$_6$H$_4$COCF$_3$, 74853-66-0; 3-F$_3$CC$_6$H$_4$COCF$_3$, 721-37-9; c-C$_6$H$_{12}$, 110-82-7; c-C$_5$H$_{10}$, 287-92-3; D$_2$, 7782-39-0.

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Selective Monohalogenation of Methane over Supported Acid or Platinum Metal Catalysts and Hydrolysis of Methyl Halides over γ-Alumina-Supported Metal Oxide/Hydroxide Catalysts. A Feasible Path for the Oxidative Conversion of Methane into Methyl Alcohol/Dimethyl Ether[1]

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Abstract: The catalytic monohalogenation (chlorination and bromination) of methane was achieved over either supported solid acid (such as FeO$_x$Cl$_y$/Al$_2$O$_3$, TaOF$_3$/Al$_2$O$_3$, NbOF$_3$/Al$_2$O$_3$, ZrOF$_2$/Al$_2$O$_3$, SbOF$_3$/Al$_2$O$_3$, SbF$_5$/graphite, and Nafion-H/TaF$_5$) or platinum metal (Pt/Al$_2$O$_3$ and Pd/BaSO$_4$) catalysts. The reactions were carried out at temperatures between 180 and 250 °C, with GHSV of 50–1400 giving 8–58% conversions with selectivity in methyl chloride (bromide) generally exceeding 90%. Limited methylene halide formation accompanies the reactions, but no formation of haloforms or carbon tetrahalides was observed. The mechanism of the halogenations is considered to involve insertion of a surface-coordinated electrophilic halogen species or electron-deficient metal site into a methane C–H bond involving five-coordinate intermediate carbonium ion formation, with subsequent cleavage–halogenolysis giving the monohalogenated methane. Catalytic hydrolysis of methyl halides was also studied over γ-alumina-supported metal oxide/hydroxide catalysts, giving mixtures of methyl alcohol and dimethyl ether. Combining the selective monohalogenation of methane with subsequent hydrolysis and oxyhalogenative recycling of byproduct HX allows conversion of methane to methyl alcohol/dimethyl ether, a route which offers an alternative to the presently exclusively used preparation of methyl alcohol via syngas. The preparation of methyl halides and/or methyl alcohol/dimethyl ether directly from methane also offers a way to convert methane via previously described bifunctional acid–base-catalyzed condensation into ethylene and subsequently into homogeneous lower olefins and/or higher hydrocarbons.

Recently there has been a revival of interest in "C$_1$ chemistry"[2] mostly utilizing syngas (i.e., mixtures of CO and H$_2$ produced from coal or natural gas) aiming at devising economical processes to manufacture hydrocarbons. An innovative new process for the