the triplet energy transfer rate constants are consistently much lower. This is still true even if a small component of the singlet rate constant is removed as a contribution from dipole–dipole energy transfer. Furthermore, the steric factors are consistently larger for triplet energy transfer, where the observed ratios of k_{et} approximate the calculated value of 6.3.[8] Of the three possible reasons we postulated earlier,[8] the incorporation of an additional mechanism (dipole–dipole) into the rate constant for singlet energy transfer is seen to provide only a partial explanation. The remaining two explanations remain as viable possibilities for future investigation. (1) Triplet energy transfer may involve a spin statistical factor, which restricts the reactivity of the three triplet sublevels.[23,37] (2) For triplet energy transfer, electron-exchange coupling may require more specific interactions of the appropriate orbitals, either in terms of the extent or orientation of orbital overlap.

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(37) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 708.

Type II Photoelimination from α-Cycloalkylacetophenones and a Polystyrene-Bound Analogue†

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Abstract: In order to evaluate the effects of polymer binding on photoreactivity and other photochemical properties, we have synthesized α-cyclohexyl-*p*-methylacetophenone (I), α-cyclopentylacetophenone (II), and an analogue bound to insoluble polystyrene beads (P-I). All undergo type II photoelimination and are effective in energy transfer to an added quencher, *trans*-stilbene. Quantitative comparisons show that the polymer binding has little effect upon the photoreactivity as long as the polymer is in a swelling solvent, such as pentane, which allows the necessary molecular flexibility. The efficiency of energy transfer is somewhat reduced upon polymer binding.

Covalent binding of reagents and substrates to insoluble polymers has been a relatively recent development which has proved to be extremely valuable for synthetic[3–6] and mechanistic work.[7–9] In particular, photochemical studies have provided useful probes of molecular mobility and flexibility within polymeric systems.[10,11] We have begun an investigation of the possible use of polymer-bound photosensitizers in solar energy schemes. Earlier studies of polymer-bound photosensitizers have illustrated their utility; in many cases they are more advantageous than homogeneous photosensitizers.[5,12–15] Fixing the light-absorbing sensitizer on an insoluble polymer support provides the usual advantages associated with polymer-bound reagents, such as ease of separation and replacement of the different components, localization of the sensitizer, and minimization of interactions with other components of the system localized elsewhere. The particular advantage which we visualize for a polymer-bound photosensitizer is that this approach will allow the use of combinations of sensitizers. With different sensitizers fixed at different locations and unable to diffuse together, it is possible to avoid energy transfer from one sensitizer to another. In homogeneous solution, diffusional energy transfer from one sensitizer to another of lower excitation energy amounts to a degradation and wastage of part of the absorbed photon energy.

In order to function as an effective photosensitizer, the sensitizer must absorb well and transfer energy efficiently to the photoactive molecule of interest. Our first investigations, reported here, thus address the effects of polymer binding upon the spectroscopy, the photochemistry, and the energy transfer capabilities of a typical organic chromophore. We chose to study a photoreactive sensitizer because the photoreaction provides a convenient monitor for any changes in the nature of the excited state or the ability to quench that excited state. We selected the type II photoelimination reaction of aromatic ketones for several reasons: (1) It is an extremely well-characterized photoreaction, both in terms of its normal mechanism as well as the effects of different solvents and substituents.[16,17] (2) As such, it has been successfully used as a sensitive probe of microenvironments in micelles and monolayers.[18,19] (3) Excited state lifetimes are generally short but readily quenchable.[16] (4) As an elimination reaction, the photoreaction can be arranged to release a small molecule from a polymer-bound ketone (as P-I, below).

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† Dedicated to George S. Hammond on the occasion of his 60th birthday.

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(3) Crowley, J. I.; Rapoport, H. *Acc. Chem. Res.* **1976**, *9*, 135–44.
(4) Jones, J. B., Ed. "The Solid Phase Methods"; Wiley-Interscience: New York, 1976.
(5) Neckers, D. C. *CHEMTECH* **1978**, *8*, 108–16.
(6) Shea, K. J.; Thompson, E. A.; Pandey, S. D.; Beauchamp, P. S. *J. Am. Chem. Soc.* **1980**, *102*, 3149–55.
(7) Rebek, J.; Gavina, F. *J. Am. Chem. Soc.* **1975**, *97*, 3453–6.
(8) Regen, S. L.; Besse, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 4059–63.
(9) Mazur, S.; Jayalekshmy, P. *J. Am. Chem. Soc.* **1979**, *101*, 677–83.
(10) Guillet, J. E. *Pure Appl. Chem.* **1977**, *49*, 249–58.
(11) Farid, S.; Martic, P. A.; Daly, R. C.; Thompson, D. R.; Specht, D. P.; Hartman, S. E.; Williams, J. L. R. *Pure Appl. Chem.* **1979**, *51*, 241–59.
(12) Schaap, A. P.; Thayer, A. L.; Blossey, E. C.; Neckers, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 3741–5.
(13) Hautala, R. R.; Little, J.; Sweet, E. M. *Sol. Energy* **1977**, *19*, 503–508.
(14) King, R. B.; Sweet, E. M. *J. Org. Chem.* **1979**, *44*, 385–91.
(15) Asai, N.; Neckers, D. C. *J. Org. Chem.* **1980**, *45*, 2903–7.
(16) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168–77.
(17) Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259–70.
(18) Turro, N. J.; Liu, K.-C.; Chow, M.-F. *Photochem. Photobiol.* **1977**, *26*, 413–5.
(19) Worsham, P. R.; Eaker, D. W.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 7091–3.

Experimental Section

α-Cyclohexyl-*p*-methylacetophenone (I). Cyclohexylacetic acid (Fluka) was converted to its acid chloride by refluxing for 45 min with excess thionyl chloride. The acid chloride was collected by distillation: bp 187 °C; yield 89%. In a three-neck flask equipped with reflux condenser and addition funnel and protected by $CaCl_2$ drying tubes were placed 80 mL of sodium-dried toluene and 20 g of sublimed $AlCl_3$. A small amount of cyclohexylacetyl chloride was added with gentle heating until evolution of HCl was evident. The remainder of the acid chloride (total 20 g, 0.12 mol) was added over 30 min, then the mixture was refluxed for 45 min. After being cooled, the reaction mixture was poured slowly into water with stirring. The yellow upper layer was washed twice with 10% NaOH and twice with water, then dried over $MgSO_4$ and distilled. Product I was collected at 210 °C (0.1 torr), solidified, and recrystallized from ethanol/water as fluffy white crystals: mp 44–45 °C; yield 12.6 g (47%); IR (C=O at 1700 cm^{-1}, aromatic C=C at 1610 cm^{-1}, para C-H bend at 820 cm^{-1}); NMR (aryl) δ 7.0 and 7.7 (4 H, $J = 9$ Hz, AB pattern), (benzyl methyl) δ 2.1 (3 H, s), (α-methylene) δ 2.5 (2 H, d, $J = 7$ Hz), (cyclohexyl) δ 0.7–1.7 (11 H, br m); UV, $\epsilon = 6300$ at $\lambda_{max} = 270$ nm, $\epsilon = 700$ at $\lambda = 350$ nm shoulder. Anal. ($C_{15}H_{20}O$)C, H.[20]

α-Cyclopentylacetophenone (II). Cyclopentylacetic acid was prepared from cyclopentyl bromide by a malonic ester synthesis and converted to its acid chloride by a procedure analogous to that described above; bp 110–113 °C (20 torr). Friedel–Crafts acylation on benzene was similar to the procedure for the synthesis of I described above, giving product II as a colorless liquid in 61% yield (from cyclopentylacetic acid); bp 170–174 °C (0.8 torr). Anal. ($C_{13}H_{16}O$)C, H.[20]

Ethyl α-Cyclohexylacetate. The ethyl ester was prepared from 4 g of cyclohexylacetic acid, 10.5 mL of absolute ethanol, 20 mL of sodium-dried benzene, and 1.9 mL of concentrated H_2SO_4. After 5 h of reflux, the lower layer was extracted with ether, combined with the upper layer, and distilled; yield 82%.

Polystyrene-Bound α-Cyclohexylacetophenone (P-I). Polystyrene beads crosslinked with 3% *p*-divinylbenzene (Aldrich) were thoroughly washed prior to use.[21] Treatment of the beads was essentially as described by Hautala.[13] A mixture of 60 mL of 15% *n*-butyllithium in hexane (Aldrich), 15 mL each of dry, deoxygenated cyclohexane and hexane, and 4.3 g of distilled tetramethylethylenediamine were stirred under N_2 for 30 min. To this solution was added 5 g of the polystyrene beads in 50 mL of dry, deoxygenated cyclohexane. The beads turned orange and were stirred under N_2 at 50 °C overnight, then washed with dry, deoxygenated THF in a dry bag, during which time the beads turned red. The beads were stirred in 25 mL of dry, deoxygenated THF under N_2 and 4.0 g of ethyl α-cyclohexylacetate was added. The beads, now yellow, were stirred at room temperature under N_2 overnight. Methanol (15 mL) was added and the mixture stirred for 1 h. The beads, now essentially white, were filtered and washed with THF in a Soxhlet extractor for 8 h, then dried in a vacuum oven at 100 °C overnight.

Quantum Yield Measurements. Samples were prepared in 13 × 100 mm Pyrex culture tubes, previously cleaned and constricted. The samples were degassed through four freeze–pump–thaw cycles to an ultimate pressure of 10^{-2} torr and sealed. Irradiations were performed in a Caltech "merry-go-round" actinometry apparatus,[22] using a Hanovia 450 W medium-pressure mercury lamp with Corning glass filters for 366-nm irradiation. A large surrounding water bath kept the temperature below 30 °C at all times. The actinometer was benzophenone–benzhydrol.[23] Samples were 0.05 M in ketone in either pentane or ethanol as solvent. Evolution of cyclohexene (from I or P-I) or cyclopentene (from II) was determined as a function of irradiation time by gas chromatographic analysis relative to an internal standard of 0.05 M *n*-decane. A correction for the amount of light absorbed by each ketone was calculated by measuring the absorbance of the sample times the transmittance of the filter at 2-nm intervals and summing that product over the effective range of the filter. Relative to the actinometer, I absorbed 80.7% of the incident light and II absorbed 94.0% of the incident light. Light absorption by P-I could only be estimated because of the large amount of scattering, because the photolysis cells were partially collapsed (to about 5 mm path length) to allow the use of lesser amounts of polymer, and because the polymer sample did not entirely block the light path. A rough estimate of 50% light absorption was used to estimate the quantum yields from P-I.

Quenching Studies. Identical solutions were prepared containing 0.05 M ketone and different concentrations of *trans*-stilbene: 0, 5 × 10^{-5}, 2.5 × 10^{-4}, or 5 × 10^{-4} M. Irradiation and analysis were performed as described above.

Scheme I

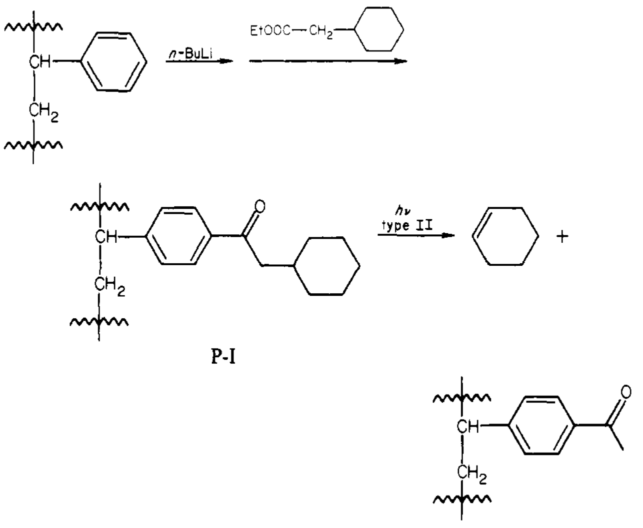


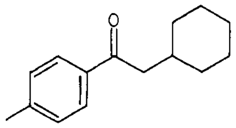
Table I. Type II Photoreactions: Quantum Yields, Stern–Volmer Quenching Constants, and Triplet Lifetimes

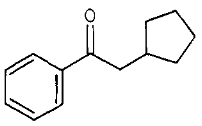
ketone	solvent	Φ	$k_q\tau$ ($\times 10^{-3}$, M^{-1})[a]	τ ($\times 10^{6}$, s)[b]
I	pentane	0.59	11.6	0.39
I	ethanol	0.25	2.5	0.42
II	pentane	1.0	1.5	0.05
II	ethanol	0.45	1.5	0.25
P-I	pentane	0.5	4.0	
P-I	ethanol	0.0		

[a] *trans*-Stilbene quenching. [b] Calculated triplet lifetimes based upon an assumption of diffusion-controlled quenching.

Results

The monomeric ketones α-cyclohexyl-*p*-methylacetophenone (I) and α-cyclopentylacetophenone (II) were prepared by Friedel–Crafts acylations.


I


II

The polymer-bound analogue of I (P-I, polystyrene–copoly(*p*-divinylbenzene) (3%)–copoly(*p*-(cyclohexylacetyl)vinylbenzene) (6%)), was prepared from 3% cross-linked polystyrene by the general procedure of Hautala[13] (Scheme I). An incorporation level of 6% for the ketone group was calculated from exhaustive irradiation experiments (up to 100 h) which gave a limiting value of 6 mol % cyclohexene released. This is a minimum determination of the level of functionalization, since there may be some photoreaction which does not release cyclohexene. Such reactions are minimal for I, however, and therefore they are not considered significant for P-I.

Quantum yields for the type II photoelimination reactions were determined by monitoring cyclohexene evolution from I and P-I and cyclopentene evolution from II. In addition, the type II photoelimination was quenched by additions of *trans*-stilbene, from which quenching constants ($k_q\tau$) were obtained by the usual Stern–Volmer analysis. The results are summarized in Table I.

Discussion

Quantum Yields. The type II photoelimination of aryl ketones involves two key intermediates, the n,π* triplet state and the 1,4-hydroxybiradical, both of which are quite sensitive to sub-

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(20) Elemental analyses performed by the Caltech Analytical Facility, Pasadena, Calif.

(21) Hartley, F. R.; Vezey, P. N. *Adv. Organomet. Chem.* **1977**, *15*, 197.

(22) Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245–9.

(23) Moore, W. M.; Ketchum, M. *J. Am. Chem. Soc.* **1962**, *84*, 1368–71.

stituent, solvent, and steric effects which can alter their partitioning and thereby affect the observed quantum efficiency.[16] In the presence of electron-donating substituents or polar solvents, the lowest energy triplet state becomes π,π^* in nature.[24] Although the π,π^* triplet state is considered to be essentially unreactive, significant photoreactivity is still observed as long as the reactive n,π^* triplet is accessible by thermal equilibration.[17,25]

The reduced quantum efficiency for I in ethanol ($\Phi = 0.25$) relative to pentane ($\Phi = 0.59$) suggests that the lowest triplet state of I is π,π^* in ethanol. Since the reduction in quantum yield is larger than normally observed,[24] it may also be the case that there are additional conformational or hydrogen-bonding effects which disfavor the reaction in ethanol.

Conformational factors play an important role in the hydrogen abstraction step; not only must the γ-hydrogen and the excited carbonyl oxygen be physically close, they must be oriented so that the electron-deficient n orbital is directed at the γ-hydrogen.[26] For example, cyclohexyl phenyl ketone undergoes no intramolecular hydrogen abstraction at all.[27] The presence of an additional methylene group, as in I, allows sufficient flexibility to permit ready access of the excited carbonyl to the γ-hydrogens. Molecular models show that for compound I, an equatorial ketone group can easily attain the desired "in-plane" orientation with either the axial (cis) or the equatorial (trans) hydrogens on the adjacent ring position (γ to the carbonyl). Comparable molecular models for II show that the only γ-hydrogens reasonably available to the excited carbonyl are those at the adjacent cyclopentane ring position in the cis orientation. These hydrogens, however, can attain a conformation even closer to the excited carbonyl than in I. This conformational effect can explain the higher quantum efficiency for II, relative to I. Other reported cases of type II reactivity of cyclic and bicyclic aryl ketones have indicated that the stereochemical positioning of the γ-hydrogen can significantly increase or decrease reactivity.[27,28]

Polymer binding of I (P-I) causes no substantial change in the photoreactivity in pentane solvent ($\Phi \sim 0.5$), which indicates that the molecules still have the necessary flexibility to attain the desired conformation for hydrogen abstraction. This is consistent with other studies of type II reactions of polyketones which indicate that quantum yields in polymer matrices are comparable to those in homogeneous solution as long as the polymer is above its glass transition temperature (i.e., there is sufficient "free volume" to allow solution-like flexibility).[10,29] The cross-linked polystyrene beads used in this study are highly swollen in pentane solvent, indicating a large free volume. Furthermore, since the functionalization of the polystyrene beads was accomplished with solution-phase reagents in a swelling solvent, all the sites which are functionalized should be accessible to solvent and within the regions of free volume. The lack of observed reactivity of P-I in ethanol solvent is probably caused by the lack of any significant swelling of the polymer beads in this solvent; in this case, the lack of free volume restricts flexibility and restricts photoreactivity. Other factors may also contribute, such as the larger disparity in refractive index between polystyrene and ethanol, which would lead to greater light reflection.

Quenching Constants. *trans*-Stilbene is a very effective quencher, causing a significant decrease in the quantum yield for type II elimination from I, II, or P-I at concentrations around 10^{-4} M. Since the triplet energy level of *trans*-stilbene (50 kcal/mol)[30] is substantially below that expected for I or II (approximately 70 kcal/mol, based upon *p*-methylvalerophenone, $E_T \sim 73$ kcal/mol[24]), the quenching should be triplet–triplet energy transfer. Furthermore, we find that irradiation of I and *trans*-stilbene drives the stilbene toward a photostationary state (~50% cis) which is characteristic of a high-energy triplet sensitizer.[31] For such an exothermic triplet–triplet energy transfer, a diffusion-controlled rate is typical.[32,33] Based on this assumption and diffusional rate constants for pentane and ethanol calculated from the modified Debye equation,[33,34] triplet lifetimes may be estimated as shown in Table I.

The triplet lifetime of I is relatively long, about 0.4 μs, in both pentane and ethanol, which suggests a lowest triplet state of π,π^* nature in both solvents. The decreased quantum yield in ethanol would be caused by a larger energy gap between the lowest π,π^* triplet and the reactive n,π^* triplet as discussed in the previous section. The short triplet lifetime of II in pentane suggests a highly reactive n,π^* triplet as the lowest triplet state in that solvent. Both the longer lifetime and diminished reactivity of II in ethanol indicate that the lowest triplet state of II is π,π^* in that solvent.

Polymer binding of I leads to a reduction in the observed quenching constant by nearly a factor of 3. While this could be attributed to a proportionally shorter triplet lifetime for P-I, relative to I, it seems more likely that a reduced rate constant is the more important contributing factor. For example, quenching of naphthalene fluorescence by a polyketone by energy transfer is found to proceed at one-third the diffusion-controlled rate.[35]

In summary, we have found that polymer binding of a photoreactive sensitizer leads to photoreactivity comparable to that for a model compound in homogeneous solution. In order to maintain this photoreactivity, however, it is necessary to use a solvent which swells the polystyrene beads and thereby provides free volume for the necessary molecular flexibility. Energy transfer from the polymer-bound photosensitizer is somewhat reduced, probably due to a reduction in the diffusional quenching rate constant.

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[24] Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604–14.

[25] Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8474–5.

[26] Turro, N. J.; Weiss, D. S. *J. Am. Chem. Soc.* **1969**, *90*, 2185–6.

[27] Padwa, A.; Eastman, D. *J. Am. Chem. Soc.* **1969**, *91*, 462–7.

[28] Padwa, A. *Acc. Chem. Res.* **1971**, *4*, 48–57.

[29] Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 212–6.

[30] Bylina, A.; Grabowski, Z. R. *Trans. Faraday Soc.* **1969**, *65*, 458.

[31] Lamola, A. A. "Energy Transfer and Organic Photochemistry"; Wiley-Interscience: New York, 1969; pp 60–70.

[32] Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769–77.

[33] Saltiel, J.; Shannon, P. T.; Zafiriou, O. C.; Uriarte, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6799–808.

[34] Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: London, 1970; p 422.

[35] Heskins, M.; Guillet, J. E. *Macromolecules* **1970**, *3*, 224–31.