# Photochemistry of Ketone Polymers. III. Energy Transfer in Ethylene–Carbon Monoxide Polymers

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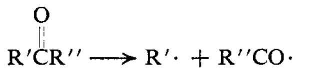
ABSTRACT: Studies have been made of electronic energy transfer to and from the excited states of carbonyl groups in ethylene–carbon monoxide copolymers in decahydronaphthalene solution and in the solid phase. The results were compared with those obtained using 6-undecanone as a model ketone. The partition of photochemical reaction between singlet and triplet precursors was examined by the use 1-*cis*,3-*cis*-cyclooctadiene as a triplet quencher. About 50% of the photochemical reaction in the carbonyl copolymer originated from the triplet state as compared with 55% in the case of 6-undecanone. Studies of the quenching of naphthalene fluorescence by carbonyl groups were used to determine energy transfer rate constants, $k_q$, and the probability of reaction during collision. These data were used to estimate the lifetimes of the ketone carbonyl triplet of 6-undecanone in solution ($\tau = 0.34 \times 10^{-8}$ sec) and for the carbonyl copolymer in solution ($\tau = 1.4 \times 10^{-8}$ sec) and in the solid phase ($\tau = 1.0 \times 10^{-8}$ sec). The rate constant for exchange energy transfer, $k_q$, is about one-third the value of $k_{\mathrm{diff}}$ calculated from the diffusion constants using the Smoluchowski equation, indicating that only about one collision in three is effective. The significance of these results on the feasibility of using energy transfer as a means of inhibiting photochemical degradation is considered.

The photodegradation of polymers such as polyethylene is often attributed to the presence of absorbing groups incorporated in the polymer during manufacture or processing. One of the more common of these is the carbonyl group which absorbs light of wavelengths reaching the earth from the sun and can undergo a variety of photochemical reactions.

Copolymers of ethylene and carbon monoxide may be considered to be polyethylene chains with carbonyl groups randomly situated along the main chain. It has been shown[2] that the photochemical reactions of such polymers when irradiated with light of wavelength 313 nm are those which occur in simple dialkyl ketones. The Norrish type I reaction leads to the formation of two free radicals. In solution these radicals will usually

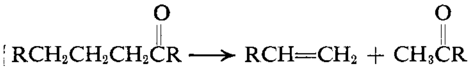


$$\mathrm{R'\overset{\displaystyle O}{\overset{\|}{C}}R''} \longrightarrow \mathrm{R'\cdot + R''CO\cdot}$$

abstract hydrogen from the solvent to form solvent radicals, which will terminate by mutual recombination or disproportionation. The type II reaction leads to

$$\mathrm{R\cdot + SH \longrightarrow RH + S\cdot}$$
$$\mathrm{S\cdot + S\cdot \longrightarrow SS}$$

$\beta$ scission with the formation of an olefin and a lower ketone. When the carbonyl group occurs in the backbone of the polymer chain, both reactions lead to a reduction in molecular weight.



$$\mathrm{RCH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}R} \longrightarrow \mathrm{RCH{=}CH_2 + CH_3\overset{\displaystyle O}{\overset{\|}{C}}R}$$

It is expected that these photochemical reactions will originate from either the lowest singlet or lowest triplet excited states of the carbonyl and a study of these states in the copolymer should help in the understanding of the photodegradation of polyolefins and other polymers which might be expected to form ketone groups by air oxidation.

One of the more fruitful methods of studying such reactions has been by means of energy exchange experiments. In these experiments the light absorbed by one molecule is transferred to another and by a study of the concentration dependence of a suitably chosen excitation acceptor, information regarding the excited state which is the precursor to photochemical reaction and the lifetime of that excited state may be deduced.[3]

In the absence of specific interactions, there are two possible mechanisms by which this energy transfer may occur. These are resonance energy transfer and exchange transfer. The former has been found to be unimportant in systems containing simple aliphatic ketones[4] although in diethyl ketone–metalloorganic systems, the mechanism is uncertain,[5] and resonance energy transfer has been invoked to explain the results. Exchange energy transfer, on the other hand, has been demonstrated with a number of ketones. This mechanism requires overlap of orbitals and is generally considered to be collision controlled for exothermic energy transfer.[6]

We have recently reported preliminary results[7] where triplet–triplet transfer from the polymeric carbonyl group to the triplet of *cis*-1,*cis*-3-cyclooctadiene [COD] was observed in solution. It was observed that only approximately 45% of reaction originated from the triplet, and thus could be inhibited by the presence of the COD. The role of conjugated dienes as triplet quenchers is not unambiguous since it has been shown

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(2)(a) G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 165 (1968); (b) *ibid.*, **1**, 413 (1968).

(3) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

(4) J. T. Dubois and B. Stevens, "Luminescence of Organic and Inorganic Materials," John Wiley & Sons, New York, N. Y., 1962, p 115.

(5) J. C. W. Chien and W. P. Connors, *J. Amer. Chem. Soc.*, **90**, 1001 (1968).

(6) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

(7) M. Heskins and J. E. Guillet, *Macromolecules*, **1**, 97 (1968).

recently[8] that such dienes can also quench singlets even if the donor has a lower singlet energy than the diene. In our quenching experiments it was observed that not all reaction was quenched. From this we assume that the "exciplex" mechanism is not efficient compared with the triplet quenching even though both are believed to be collisionally controlled.

In order to determine the lifetime of the triplet carbonyl it is necessary to make some estimate of the rate of transfer. Although this is normally derived from viscosity[6] or diffusion measurements,[9] recent results[10–12] indicate that the actual rate of transfer may be significantly lower than this. In order to obtain an experimental measure of this, energy transfer from the naphthalene singlet to ketone singlets has been studied. This is thought to occur by an exchange mechanism and the rate of transfer can be calculated from fluorescence measurements.

## Experimental Section

**Apparatus.** The source of uv light was a A.E.I. ME/D box type mercury arc lamp. Light of 313 nm was isolated by means of Jena uv P.I.L. interference filter mounted in a brass holder and cooled by air. Analysis of the filtered light showed that greater than 85% was contained in the peak at 313 nm with small peaks at 304 and 335 nm. For the film studies a very small peak at 366 nm was filtered out by the addition of a filter of 2 cm of a solution containing 46% w/v $NiSO_4 \cdot 6H_2O$, and 14% w/v $CoSO_4 \cdot 7H_2O$ in distilled water. The light intensity from the lamp was monitored by means of an IP28 photomultiplier tube, powered by a Lambda Model 25 regulated dc power supply. Over the entrance of the photomultiplier was a gold plated quartz disk protected by a second quartz disk. This served as a neutral density filter. The signal from the phototube was recorded by means of a Leeds and Northrup Model G recorder.

For polymer photolyses in solution, the light from the lamp was collimated by means of a quartz lens, passed through the filter, photolysis cell, held in place by an aluminium block which also served to control the temperature, and then to the photomultiplier. The cell holder was heated by means of circulating oil from a Lauda Model K2 constant-temperature circulator. The lamp, lens, filter cell block, and photomultiplier tube housing were all rigidly mounted on an optical bench. The photolysis cell consisted of a cylindrical quartz tube with plane quartz end plates. The cell was 5 cm in length and 3 cm in diameter. To the filling tube was connected a side arm consisting of a bulb and capillary. This was used to determine the viscosity of the solution as the photolysis proceeded. These viscosities were performed in a water bath controlled at 80 ± 0.02°. For solution photolyses of simple ketones, a smaller cell having 2 cm path length was used.

**Materials. Polymers.** The polymers used in these studies were copolymers of ethylene and carbon monoxide polymerized by a high-pressure process. The polymers (in bead form) were samples supplied by Tennessee Eastman Co. They were extracted with Fisher Spectroquality hexane before use. The carbonyl concentration of pressed films of the copolymers were determined by infrared spectroscopy using 8-pentadecanone in hexane as a standard. The carbonyl concentration and intrinsic viscosities of these copolymers and the number average molecular weight of one of them are given in Table I.

TABLE I
PROPERTIES OF THE ETHYLENE–CARBON MONOXIDE COPOLYMERS

| Polymer | Carbonyl concn, wt % | Intrinsic viscosity, dl/g | Number average mol wt (by osmometry) |
|---|---|---|---|
| 85F | 0 | 1.07 | |
| 85G | 0.3 | 1.05 | |
| 85H | 0.55 | 1.06 | |
| 85I | 1.00 | 1.05 | 40,000 |

Intrinsic viscosities were carried out in a Desreux viscometer and determined as the common intercept of plots of ln $\eta_{rel}/c$ and $\eta_{sp}/c$ against concentration $c$. The number average molecular weight was determined with a Mechrolab 502 high speed membrane osmometer in mixed xylenes at 70° using Gel Cellophane 600 membranes.

A mixture of *cis*- and *trans*-decahydronaphthalene (decalin) was used as the solvent. It was purified by distillation and passing through a silica gel column. Before use it was filtered through a 1.0-$\mu$ millipore filter to remove suspended matter. The decalin was completely transparent at wavelengths greater than 270 nm.

The ketones, 6-undecanone and 8-pentadecanone, were prepared by Hartley[2b] and used without further purification. *cis*-1,*cis*-3-Cyclooctadiene (Aldrich) was purified on a spinning band column. Gas chromatography on two columns indicated that the cyclooctadiene was >99.9% pure. Naphthalene was purified by 40 passes of a zone refiner. Those sections which showed no impurities by gas chromatography or uv spectrum were combined and used.

**Photolyses.** For the photolysis of the copolymers in solution, a 1.8% solution of the polymer in decalin was prepared in the cell. On cooling any additive required was added and the cell sealed under vacuum after degassing with several freeze–thaw cycles using Dry Ice–acetone for freezing. The vacuum was $<10^{-3}$ Torr before sealing.

The cell was transferred to a water bath maintained at 80°, and allowed to equilibrate. The flow time of the solution through the viscometer side arm to the cell was then measured. This was repeated several times. The solvent flow time was measured in a similar manner before the beginning of the experiment. The cell was then transferred to the cell block and allowed to equilibrate for 30 min. The light beam was then allowed to enter the cell and photolysis continued for a sufficient length of time for a significant change in viscosity. The light absorbed was determined from the incident and emergent light intensities monitored by the photomultiplier before, during and after the experiment. The cell was then removed to the water bath, and, after equilibration, the solution flow time again measured. Photolysis and viscometry were repeated several times until approximately 10% decomposition of the carbonyl groups had taken place.

The limiting viscosity number $[\eta]$ was determined from the logarithmic viscosity number ln $\eta_r/c$ using the equation $\ln \eta_r/c = [\eta] - k[\eta]^2 c$ with a value of $k$ determined from plots for the original and three of the degraded polymers. Values of $k$ varied slightly with $[\eta]$ and, since all solutions were at similar concentrations, the value of $k$ used $[0.100 < k > 0.113$ for $0.6 < [\eta] > 1.05]$ was determined from a plot of ln $\eta_r$ against $k$. The number average molecular weight was obtained from the value of $[\eta]$ using the relation of

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(8) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968), and references cited therein.

(9) R. M. Noyes, *Progr. Reaction Kinetics*, **1**, 129 (1961).

(10) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(11) P. J. Wagner, *ibid.*, **89**, 5715 (1967).

(12) D. I. Schuster, A. C. Fabian, N. P. Kong, W. C. Barringer, W. V. Curran, and D. H. Sussman, *ibid.*, **90**, 5027 (1968).

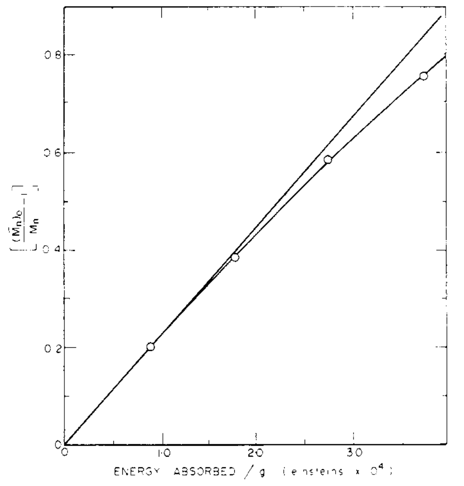

Figure 1. Plot of $[((\bar{M}_n)_0/M_n) - 1]$ as a function of light absorbed for a 1.8% solution of 1% CO copolymer in decalin solution at 80°.

TABLE II
NUMBER AVERAGE MOLECULAR WEIGHT OF 1% CARBONYL COPOLYMER AND SOME PHOTOLYZED POLYMERS

| | Molecular weight ($\bar{M}_n$) | |
|---|---|---|
| Polymer | By osmometry | Viscosity |
| 851 | 40,000 | 44,500 |
| MP6 | 28,000 | 30,500 |
| MP3 | 23,000 | 24,000 |
| MP2 | 23,000 | 23,000 |

Uberreiter, *et al.*[13] ($[\eta] = 3.875 \times 10^{-4} M_n^{0.735}$). The number average molecular weight of four samples of this copolymer determined by osmometry in mixed xylenes at 70° with a Mechrolab high speed membrane osmometer are compared with those obtained from viscometry using this equation in Table II. The quantum yield for chain scission was obtained by plotting the quantity $[(\bar{M}_n)_0/\bar{M}_n) - 1]$ as a function of the light absorbed per gram of polymer. This quantity represents the average number of bonds broken per original copolymer molecule. A typical plot is shown in Figure 1. It can be seen that the slope is initially constant but tends to decrease as the photolysis proceeds. This could be due to secondary reactions of the primary products or to changes in polydispersity. Both of these factors can be eliminated by evaluating the quantum yield from the limiting slope.

By dividing the slope obtained from such a plot by $(\bar{M}_n)_0$ we may calculate the quantum yield of chain breaks, $\phi_0$. For this experiment the quantum yield is $\phi_0 = 0.050 \pm 0.003$.

**Film Measurements.** Films were compression molded from the hexane-extracted beads in a Carver press for 1 min at 15,000 psi. The films were rapidly quenched by passing cold water through the press. Various concentrations of COD were incorporated into the film by soaking the film in COD for 24 hr at different temperatures. The films were then wiped free of surface additive and clamped between two quartz plates and placed in a special cell. The cell was pressurized to 50 psi of nitrogen to ensure minimum loss of COD from the films. The film was then irradiated for a convenient length of time after which the film was extracted with pentane to remove the COD, which was determined spectrophotometrically to estimate the concentration of COD originally present in the film. The concentration of vinyl groups in the extracted film was determined by the method of Hartley and Guillet[1] after drying under vacuum at room temperature. The above sequence was repeated three to four times for each film using the same area for irradiation in successive measurements.

**Photolysis of 6-Undecanone.** A cylindrical quartz cell of 2.0 cm path length was used and solutions of 0.1 *M* in ketone with any additive necessary were degassed and sealed in a manner similar to that described for polymer solutions. The solutions were photolysed under vacuum to about 5% decomposition of the ketone, then analyzed on a Perkin-Elmer Model 800 gas chromatograph using $^1/_8$ in. × 5 ft columns of 5% w/w silicone oil SE 30 on Chromosorb P. The product concentrations were determined from their peak areas measured by a disk integrating unit attached to the recorder, using an internal standard.

**Fluorescence Measurements.** For fluorescence studies in solution the cell block was modified by a hole cut at right angles to the incident beam direction. Light emerging from the cell in this direction was focused on the entrance slit of a Jarrell-Ash 82-A10 grating monochromator. On emergence from the monochromator the light was monitored by a IP28 photomultiplier powered by a Harrison Model 6515A dc power supply operating at 600 V.

The solutions were prepared in a manner similar to those described above except that the solution had a constant naphthalene concentration and varying concentrations of polymer or ketone. The fluorescence of the solutions were scanned over the wavelength range 290–400 nm.

For measurements in the solid film the film cell was fixed at an angle 30° to the incident beam and the Jarrell-Ash monochromator at a further 15° to the beam direction. Naphthalene was introduced by allowing the film to soak in a solution of 1 *M* naphthalene in hexane. After wiping the surface naphthalene off, the hexane was allowed to evaporate for 1 hr. Emission intensity was reproducible by this technique to ±5%. The concentration of naphthalene on the film was 0.6 *M* as determined by spectrophotometry of hexane extracted films. No excimer emission from the naphthalene was observed.

## Results and Discussion

**Triplet Quenching of Polymer Photolysis in Solution.** 1,3-Cyclooctadiene (COD) was used for triplet quenching studies. It absorbs very weakly at 313 nm ($\epsilon_{313} = 0.03$) and is a tail to the main absorption peak at 228 nm. Its triplet level is not known but has been placed at approximately 70 kcal/mol[14] based on the fact that it accepts triplet energy from acetophenone. Since the triplet levels of aliphatic ketones are expected to be greater than that of acetophenone, energy transfer between the polymeric ketone and COD should also be efficient.

In experimental studies of electronic energy exchange it is convenient to express the experimental results in the form of a Stern–Volmer equation of the form

$$\frac{\phi_0}{\phi} = 1 + k_q\tau[\mathrm{Q}]$$

where $\phi_0$ is the quantum yield for a particular process in the absence of a quenching molecule, $\phi$ is the quantum yield of the quenched process, $k_q$ is the bimolecular rate constant for the quenching process, $\tau$ is the lifetime of the state in the absence of quencher, and [Q] is the

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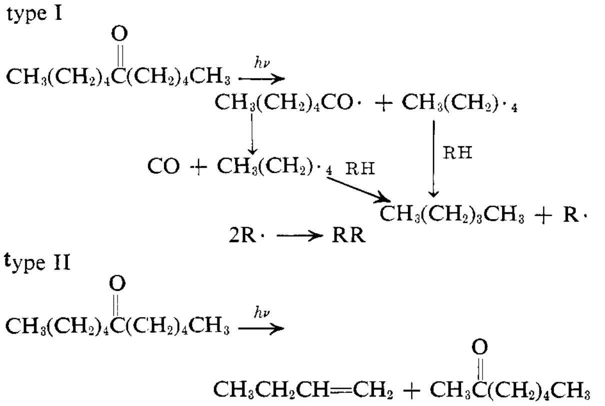
[13] K. Uberreiter, H. J. Orthman, and S. Sorge, *Makromol. Chem.*, **8**, 21 (1952).

[14] R. S. H. Liu, *J. Amer. Chem. Soc.* **89**, 112 (1967).

concentration of the quenching molecule. Data on the quenching of the photolysis of the ethylene–carbon monoxide copolymer by COD have been reported in a previous communication.[7] The Stern–Volmer plot is curved and reaches a limiting value which indicates that under the conditions of the experiment, only 45% of the total reaction arises from the triplet state, and can be quenched by COD. When allowance is made for this, the curve shown in Figure 2 is obtained. From the limiting slope of this curve a value of $k_q\tau$ = 20 l. mol$^{-1}$ is obtained.

**Triplet Quenching of 6-Undecanone Photolysis.** There are no reports of quenching studies on higher symmetrical dialkyl ketones so the effect of COD on the photolysis of a low molecular weight homolog of the polyketone, 6-undecanone (dipentyl ketone), was also studied for comparison with the polymer data.

The photochemical reactions of 6-undecanone upon irradiation with 313-nm light can be represented by the following equations.



type I

$$CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}(CH_2)_4CH_3 \xrightarrow{h\nu} CH_3(CH_2)_4CO\cdot + CH_3(CH_2)\cdot_4$$

$$CH_3(CH_2)_4CO\cdot \longrightarrow CO + CH_3(CH_2)\cdot_4 \xrightarrow{RH} CH_3(CH_2)_3CH_3 + R\cdot$$

$$CH_3(CH_2)\cdot_4 \xrightarrow{RH} CH_3(CH_2)_3CH_3 + R\cdot$$

$$2R\cdot \longrightarrow RR$$

type II

$$CH_3(CH_2)_4\overset{O}{\overset{\|}{C}}(CH_2)_4CH_3 \xrightarrow{h\nu} CH_3CH_2CH{=}CH_2 + CH_3\overset{O}{\overset{\|}{C}}(CH_2)_4CH_3$$

There was no evidence for formation of a cyclobutanol derivative. The type I reaction was followed by determination of pentane. No caproaldehyde was detected and it was assumed that all the acyl radicals decarbonylated at this temperature (80°). The type II product was followed by the analysis of both 1-pentene and 2-pentanone. The analyses were performed by gas chromatography and, based on the precision of the determination of the light absorbed and the reproducibility obtained in the analyses, the quantum yields are probably accurate to within 10% and reproducible to ±3%. The quantum yields for the two processes are given in Table III.

The quantum yield of type I product was reduced by the addition of COD but in view of the fact that this may have been due to addition of the radicals to the double bonds in COD, this effect cannot be considered as unequivocal evidence for quenching. The quantum yields of type II reaction $\phi_{II}$ for 6-undecanone in the presence of added COD are presented as a Stern–Volmer plot in Figure 3.

TABLE III
QUANTUM YIELDS FOR REACTION OF 6-UNDECANONE AT 80° IN DECALIN

| Reaction | Product | $\phi$ |
|---|---|---|
| Type I | Pentane | 0.014 |
| Type II | 1-Butane | 0.11 |
| | 2-Heptanone | 0.11 |

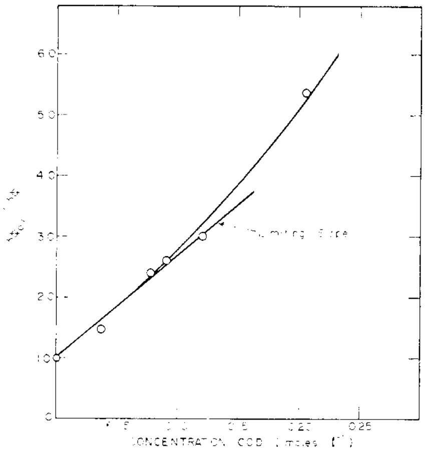


Figure 2. Stern–Volmer plot of triplet quenching of 1% CO copolymer by COD in solution at 80°.

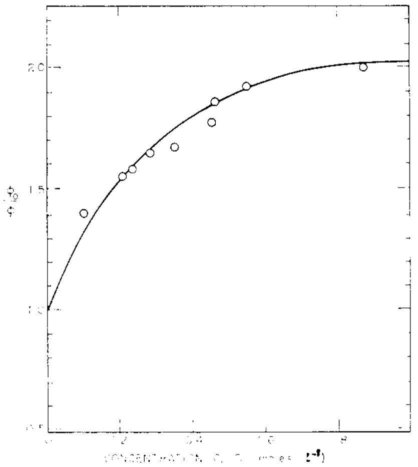


Figure 3. Stern–Volmer plot of quenching of type II reaction of 6-undecanone by COD in solution at 80°.

It can be seen that, as for the polyketone, the plot levels off and approximately 55% of the reaction originates from the triplet. When allowance is made for this, a linear relation is obtained for the quenching of type II reaction from the triplet. The value of $k_q\tau$ so determined is 10 l. mol$^{-1}$.

Values reported for the partition of excited states in the photolysis of other aliphatic ketones in solution range 60–90% reaction originating from the triplet.[15–20]

**Fluorescence Quenching by Ketones.** In order to determine the lifetime of the triplet, $\tau$ it is necessary to determine the rate constant of energy exchange $k_q$. Since $k_q$ is often considered to be diffusion controlled[6] it could be calculated from the diffusion coefficients for the reacting species. However, in view of the fact that the probability of energy transfer during a collision with a polymer molecule may be less than unity, it was desirable to make an independent estimate from data on the rather similar process involved in the quenching

(15) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).
(16) N. C. Yang and D. H. Yang, *ibid.*, **80**, 2913 (1958).
(17) F. S. Wettack and W. A. Noyes, Jr., *ibid.*, **90**, 3901 (1968).
(18) N. C. Yang and S. P. Elliot, *ibid.*, **90**, 4194 (1968).
(19) N. C. Yang and E. D. Feit, *ibid.*, **90**, 504 (1968).
(20) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

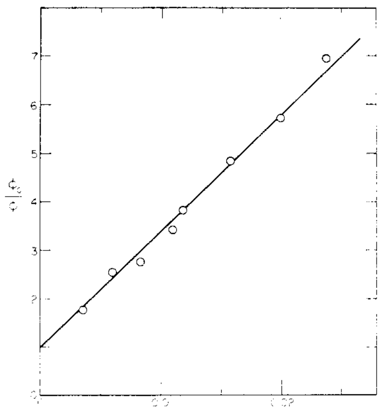


Figure 4. Stern–Volmer plot of quenching of naphthalene fluorescence by 6-undecanone in solution at 80°. Corrected for light absorbed by the ketone.

of naphthalene fluorescence, where a direct measure of the efficiency could be obtained.

Naphthalene has a similar singlet and a lower triplet level than aliphatic ketones so that both singlet–singlet (naphthalene → ketone) and triplet → triplet (ketone → naphthalene) energy exchange are possible. The former could occur by a resonance mechanism but Dubois and Stevens[4] have shown that this mechanism is not important for transfer between naphthalene and biacetyl and so it is not expected to be important here. Naphthalene is a donor which has exhibited "exciplex" transfer[8] but in the present case the ketone singlet is of lower energy than the naphthalene singlet and hence the latter mechanism will be indistinguishable from exchange transfer. There is as yet no evidence that ketones do exhibit the exciplex type of transfer and we have assumed it does not. This assumption is not, of course, central to the purpose of the present work, since our primary interest is in comparing transfer processes in small and macromolecular systems, rather than in the elucidation of a precise mechanism for the process. In view of the relatively long lifetime of naphthalene fluorescence ($1 \times 10^{-7}$ sec)[20] compared with those expected for aliphatic ketones ($7 \times 10^{-9}$ sec)[14] a naphthalene concentration was chosen where triplet → triplet transfer would be negligible. Thus the energy transfer of singlet energy from naphthalene to ketone may be followed by the decrease in fluorescence and the increase in photoreaction of the ketone.

The quenching of naphthalene fluorescence by addition of 6-undecanone was observed in samples sealed under vacuum, at 80°. The concentration of naphthalene used was 0.01 *M*, well below that at which concentration quenching is observed.[21] The quantum yields obtained were relative values (*i.e.*, emission intensity at 90° to the incident beam relative to that of naphthalene without ketone), corrected for light absorbed by the ketone. The results are plotted in Figure 4 in the form of the Stern–Volmer relation. The intensities were averaged (mean error ±2%) from measurements taken at several wavelengths where there was no scattered light from the subsidiary peaks of the filtered light from the irradiation lamp. The slope obtained from Figure 4 is 240 l. mol$^{-1}$ which is equal to $k_q\tau$ for this stytem. The lifetime, $\tau$ for fluorescence of pure naphthalene at 80° was taken as $8.5 \times 10^{-8}$ sec from the data of Magata, *et al.*[21] This leads to a value for $k_q$ of $2.8 \times 10^9$ l. mol$^{-1}$ sec$^{-1}$.

This value may be compared with that derived from the assumption that the energy exchanged is diffusion controlled. Several equations have been derived for calculating such constants from viscosity data, but the two most common are based on the derivation by Smoluchowski.[22] Although the theoretical basis of this derivation is of questionable validity,[23] it often gives values for $k_q$ which agree well with experiment.[6] In the equation derived by Smoluchowski the rate constant for a diffusion controlled process is $k_{\text{diff}} = 4\pi\rho DN/1000$, where $\rho$ is the sum of the radii of the colliding molecules, $D$ is the sum of the diffusion coefficients of the molecules in the medium, and $N$ is Avogadro's number.

In the approximation due to Debye[24] the diffusion coefficients are considered equal to that of the solvent which is then related to its viscosity $\eta$ and the equation becomes $k_{\text{diff}} = 8RT\eta/3000$. In view of the fact that later we shall be dealing with polymer solutions where viscosity and segment mobility are not directly related, we use the Smoluchowski relation for this calculation. For transfer between naphthalene and undecanone $\rho = 4 \times 10^{-8}$ cm which is equivalent to considering that only the C=O group is the reacting species in the ketone molecule and $\tau = 8.5 \times 10^{-8}$ sec. The diffusion coefficients of naphthalene and undecanone in decalin at 80° are not available, but they can be estimated from those of the straight chain hydrocarbons in decalin[25] at 25° corrected to 80° by use of the equation

$$D_{T_1} = D_{T_2}\frac{(273 + T_1)\eta_{T_2}}{(273 + T_2)\,\eta_{T_1}}$$

The value so obtained for the mutual diffusion coefficient $D$ at 80° is $1.4 \times 10^{-5}$ cm$^2$ sec$^{-1}$. Using this value in the Smoluchowski equation yields a value for $k_{\text{diff}} = 8.3 \times 10^9$ l. mol$^{-1}$ sec$^{-1}$. This is about three times the value of $k_q$ for naphthalene–6-undecanone ($2.8 \times 10^9$) obtained from the fluorescence measurements, indicating that only about one "collision" in three is effective. One may express this in terms of an efficiency factor $p$ defined by $k_q = pk_{\text{diff}}$, which gives a value of $p = 0.34$ in the above case.

In an attempt to determine if one might expect a molecular weight effect, quenching studies were carried out in aerated solutions of a variety of symmetrical aliphatic ketones at 25°. Values of $k_q$ obtained from the Stern–Volmer plots are compared in Table IV with the values of $k_{\text{diff}}$ calculated from the Smoluchowski equation using the diffusion constants measured on linear alkanes with a similar number of carbon atoms.[25] There appears to be no significant variation in efficiency for the higher ketones as the chain length is increased,

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(22) M. Smoluchowski, *Z. Phys. Chem.*, **92**, 129 (1917).

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(24) P. Debye, *Trans J. Electrochem. Soc.*, **82**, 265 (1959).

(25) R. Varoqui, M. Daune, and L. Freund, *J. Chim. Phys.*, **58**, 394 (1964).

TABLE IV
VARIATION IN EFFICIENCY OF ENERGY EXCHANGE WITH KETONE CHAIN LENGTH AT 25°

| Ketone | $k_q\tau$, l. mol$^{-1}$ | $k_q \times 10^{-9}$,[a] l. mol$^{-1}$ sec$^{-1}$ | $k_{diff} \times 10^{-9}$, l. mol$^{-1}$ sec$^{-1}$ | $p$ |
|---|---|---|---|---|
| Acetone | 105 | 2.0 | 4.2 | 0.48 |
| 6-Undecanone | 98 | 1.8 | 2.9 | 0.62 |
| 8-Pentadecanone | 91 | 1.6 | 2.5 | 0.64 |
| 12-Tricosanone | 87 | 1.5 | 2.3 | 0.64 |

[a] Using $\tau = 5.5 \times 10^{-8}$ sec for aerated solutions of naphthalene.

TABLE V
QUENCHING OF NAPHTHALENE FLUORESCENCE BY CARBONYL COPOLYMERS AT 80°

| Concn of carbonyl groups, mol l.$^{-1}$ × 10$^3$ | $\phi_0/\phi$[a] |
|---|---|
| 3.8[b] | 1.32 |
| 3.5 | 1.30 |
| 6.8 | 1.72 |
| 9.9 | 2.09 |
| 10.1 | 2.23 |
| 12.8 | 2.43 |

[a] All solutions were 0.01 *M* in naphthalene. [b] 0.55% carbonyl copolymer, all others using 1% copolymer.

TABLE VI
QUENCHING OF NAPHTHALENE FLUORESCENCE BY CARBONYL COPOLYMER CALCULATED FROM $\phi$ CHAIN BREAKS

| Carbonyl concn, mol l.$^{-1}$ × 10$^2$ | Naphthalene concn, mol l.$^{-1}$ × 10$^2$ | $\phi$ chain scission based on polymer absorption | $\phi_0/\phi$ fluorescence quenching |
|---|---|---|---|
| 0.195 | 0.0 | 0.043 | 1 |
| 0.195 | 0.5 | 0.097 | 1.15 |
| 0.337 | 0.0 | 0.049 | 1 |
| 0.337 | 0.3 | 0.109 | 1.28 |
| 0.337 | 0.5 | 0.121 | 1.29 |
| 0.65 | 0.0 | 0.051 | 1 |
| 0.65 | 0.5 | 0.088 | 1.74 |
| 0.65 | 1.0 | 0.100 | 1.58 |

but the process does appear to be more efficient at 25 than at 80°, as evidenced by a larger value of $p$.

**Quenching of Naphthalene Fluorescence by Carbonyl Copolymers.** The quenching of naphthalene fluorescence by the carbonyl copolymers was carried out by essentially the same technique as for 6-undecanone. Two polymers were used, the 1% copolymer at various concentrations and the 0.55% at one concentration. The results are given in Table V and the Stern–Volmer plot in Figure 5. Also included in Figure 5 are some results calculated from the quantum yield of chain breaks in presence of naphthalene from separate experiments. From the increase in the quantum yield of chain scission based on light absorbed by the polymer we may calculate the light absorbed by the naphthalene which is subsequently transferred to the ketone. From this, the quantum yield of fluorescence in the presence of ketone is calculated. These results are tabulated in Table VI. It is seen that the value of $\phi_0/\phi$ obtained using 0.01 *M* naphthalene does not fall on the line.

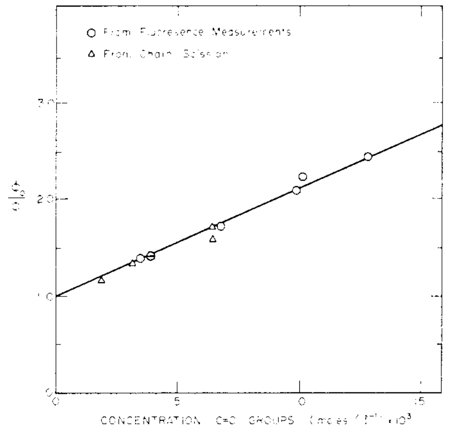

Figure 5. Stern–Volmer plot of quenching of naphthalene fluorescence by carbonyl copolymers in solution at 80°: ○, from fluorescence measurements corrected for light absorbed by polymers; the point marked ⊖ obtained using 0.55% CO copolymer, all others using 1% CO polymer; △, calculated from increases in $\phi_{\text{chain scission}}$ based on light absorbed by polymer. Using three polymers containing 0.3, 0.55, and 1% CO.

This is ascribed to the fact that naphthalene is also acting as a quencher in this case. The amount of quenching (to place the point close to the line) is similar to that observed when COD is used at this concentration.

It will also be observed that it appears that carbonyl photolysis has been sensitized. However, naphthalene absorbs much more of the light and, when breakdown is related to the incident light, the effect is much less marked.

The slope of the plot in Figure 5 is 115 ± 10 l. mol$^{-1}$ and using a figure of $8.5 \times 10^{-8}$ sec as $\tau$, $k_q = 1.4 \times 10^9$ l. mol$^{-1}$ sec$^{-1}$. In order to compare this with the value given by the Smoluchowski equation the diffusion coefficient of the polymer is required. However, it is difficult to know what segment of the polymer must be considered as the diffusing element. Two extremes can be considered, *i.e.*, negligible polymer movement compared with naphthalene or a segment diffusion coefficient comparable with that of 6-undecanone.

For the minimum value $k_{diff} = 4.15 \times 10^9$ l. mol$^{-1}$ sec$^{-1}$ from which $p = 0.33$ and for the maximum $k_{diff} = 8.3 \times 10^9$ l. mol$^{-1}$ sec$^{-1}$ which gives $p = 0.16$. These $p$ values are of the same order as for 6-undecanone at the same temperature, and we must conclude from this that the collisional efficiency for the energy exchange process in the polymer must be rather similar to that for small molecules. In fact if one assumes that the polymer does not diffuse at all, the $p$ values obtained in the two experiments are identical.

**Energy Transfer in the Solid Phase.** The success obtained in evaluating energy exchange processes for polymers in solution led to attempts to obtain similar data in the solid polymers. Studies were therefore made using polymer films containing various amounts of COD or naphthalene. In the former case, due to the fact that absorption of COD masks the vinyl group absorption in the infrared region, the type II quantum yield for the polymers could not be measured without first removing the COD. Because very little quenching was observed, the process of alternately

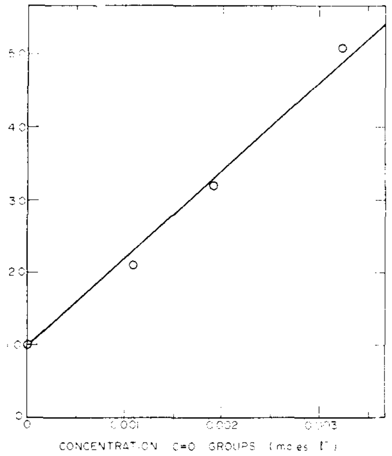

Figure 6. Stern–Volmer plot of quenching of naphthalene fluorescence by carbonyl copolymers in film form at 80°.

adding and removing COD led to large scatter in the data. Values of $\Delta K$, the increase in terminal vinyl absorption, were plotted against light absorbed for the 1% carbonyl film containing several different concentrations of COD and a least squares fit of the data to a straight line gave the quantum yields shown in Table VII. From these data, and assuming that 45% of the reaction comes from the triplet (as in solution), a Stern–Volmer plot yields a value of $k_q\tau = 3$ l. mol$^{-1}$. Films of four polymers containing 0, 0.3, 0.55, and 1% carbonyl groups were prepared to contain 0.6 *M* naphthalene. The fluorescence quenching by these polymers was measured at 350 nm and 80° and the Stern–Volmer plot is shown in Figure 6. Each point is the average of three determinations.

Table VII
Quenching of $\phi_{II}$ in Polymer Film at 80°

| Concn of COD, mol l.$^{-1}$ | $\phi_{II}$ |
|---|---|
| 0.0 | 0.033 |
| 0.107 | 0.028 |
| 0.20 | 0.026 |
| 0.39 | 0.025 |
| 0.45 | 0.021 |

From the plot $k_q\tau = 12$ l. mol$^{-1}$ and for $\tau = 8.5 \times 10^{-8}$ sec this gives $1.4 \times 10^8$ l. mol$^{-1}$ sec$^{-1}$ for $k_q$, the rate constant for energy transfer, a value about one-tenth that obtained for the polymer in solution. This lower value is undoubtedly due to the reduced mobility of the naphthalene in the solid matrix of the polymer. In fact if one assumes a constancy of the $p$ factor, one can use these data to estimate $k_{\text{diff}}$ and hence the diffusion coefficient $D$ for naphthalene in polyethylene by substitution in the Smoluchowski equation. From this calculation, a value of $1 \times 10^8$ l. mol$^{-1}$ sec$^{-1}$ is obtained for the diffusion constant of naphthalene at 80°, which compares very well with the value of $7 \times 10^7$ l. mol$^{-1}$ sec$^{-1}$ determined for octadecane in low-density polyethylene at the same temperature by radioactive tracer methods.[26]

Table VIII
Transfer Rate Constant from Fluorescence Quenching

| Ketone | Phase | $k_q\tau$, l. mol$^{-1}$ | $k_q$, l. mol$^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| 6-Undecanone | Hydrocarbon solution | 240 | $2.8 \times 10^9$ |
| Ethylene–CO copolymer | Hydrocarbon solution | 115 | $1.4 \times 10^9$ |
| Ethylene–CO copolymer | Solid film | 12 | $1.4 \times 10^8$ |

Table IX
Triplet Lifetimes of Ketone Carbonyls at 80°

| Ketone | Phase | $k_q\tau$, l. mol$^{-1}$ | $\tau$, sec |
|---|---|---|---|
| 6-Undecanone | Hydrocarbon soln | 10 | $3.4 \times 10^{-9}$ |
| Ethylene–CO copolymer | Hydrocarbon soln | 20 | $1.4 \times 10^{-8}$ |
| Ethylene–CO copolymer | Solid film | 3 | $1 \times 10^{-8}$ |

**Lifetimes of Excited States.** If we make the reasonable assumption that the efficiency factor $p$ is similar for the two energy exchange processes considered, *i.e.*, $^3$(ketone) → $^3$(COD) and $^1$(naphthalene) → $^1$(ketone) then we may estimate the lifetimes of the triplet excited states of the ketone carbonyl in various environments. We have assumed that the $p$ factor is some steric effect related to the localized nature of the oribitals of the carbonyl group in aliphatic ketones. On the basis of some solid state studies, it has been suggested[27] that there is a steric requirement for exchange energy transfer.

It is then possible to use the value of $k_q$ determined experimentally from naphthalene quenching directly in the value of $k_q\tau$ obtained from ketone quenching to obtain $\tau$. The values of the transfer rate constant $k_q$ determined from fluorescence quenching are shown in Table VIII and the values of triplet lifetimes obtained using these values of $k_q$ are shown in Table IX.

These results indicate that the lifetime of the carbonyl triplet in the polymeric ketone and the symmetrical ketone studied is very short. This conclusion is supported by the earlier finding of Hartley and Guillet,[2b] that atmospheric oxygen does not appear to quench any of the reaction and these workers concluded that, in order to observe quenching by oxygen at 90°, the lifetime must be longer than $10^{-7}$ sec.

Methyl ketones are also reported to have short triplet lifetimes.[15,18,19] It will be noted that on increasing the chain length, the lifetime increases while the quantum yield decreases. This implies that the quantum yield is not controlled by other processes competing with the type II reaction from the triplet state. This conclusion would appear to support the biradical mechanism of Yang and Yang[16] as applied to the type II mechanism by Wagner and Hammond[15] and Wagner.[11] However, it is implicit in that mechanism that the quantum yield does not change with increasing chain length, although anomalous effects of chain

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length have been observed in the type II reaction of alkyl phenyl ketones.[28,29] This question will be considered in a subsequent communication.[30]

## Conclusions

From these experiments it appears that the processes of electronic energy transfer in polymeric ketone systems both in solution and in the amorphous bulk phase above $T_g$ are rather similar to those observed with smaller molecules. The lifetimes of the excited states appear to be of the same order of magnitude and the collisional efficiency for energy exchange nearly identical. Bimolecular processes involving reaction from excited states will be altered in polymer systems primarily by the difference expected in the diffusion rates of interacting species, particularly in the bulk phase.

The utility of energy transfer processes for the stabilization of polymers will depend to a large extent on the lifetime of the excited states involved. In the present instance involving aliphatic carbonyl groups, the excited state lifetimes, $\tau$, are so short that excessive concentrations of the stabilizer molecules would be required to obtain an economically desirable effect. However, other polymers, particularly those containing phenyl groups, might be expected to have longer lifetimes and hence would be easier to stabilize by this mechanism. In view of this, the study of energy transfer processes in other polymers may well lead to important advances in the development of stabilizer systems.

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# Diffusion-Controlled Oxidative Degradation of Isotactic Polystyrene at Elevated Temperatures.
## I. Experimental Procedure and Results

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ABSTRACT: The thermal-oxidative degradation of isotactic polystyrene has been studied in closed quartz spoon gauge reaction vessels over a temperature range from 249 to 300°. Changes in initial gas pressure, oxygen consumption, hydroperoxide formation, volatile formation, chain scission, and uv spectra were measured as a function of temperature and initial oxygen pressure. Chromatography showed that volatiles consist mainly of water during the initial stage of degradation. The residues of isotactic and atactic polymer, respectively, were also investigated by chromatography after prolonged oxidation. The value for the energy of activation for oxygen consumption and the dependence of the degradation on polymer film thickness indicate that the oxidation process is diffusion controlled.

Aspects of oxidative degradation of polystyrene have been studied repeatedly. Work published before 1955 was reviewed by Jellinek[1] and the relevant literature up to about 1962 was discussed by Tryon and Wall.[2] A review article and a book on oxidative degradation of polyolefins appeared recently by Reich and Stivala.[3] A book by Neiman[4] and a chapter by Jellinek[5] in a recent book on stereospecific polymers are relevant in this connection. Nmr, uv, and ir spectra during oxidative degradation were obtained and discussed by Beachell and Smiley.[6]

A comprehensive investigation of the oxidative degradation of isotactic polystyrene, taking into account a number of relevant parameters of importance for the process, does not appear to have been carried out. Such parameters are, for instance, oxygen consumption, peroxide formation, chain scission, volatile formation, reactions at side groups, change in spectra, etc. In 1949, Jellinek[7] studied the oxidative degradation of atactic polystyrene, but only from the standpoint of chain scission.

It seems to be generally agreed that initiation of the oxidative process in the case of polystyrene is due to abstraction of tertiary hydrogen atoms. The polymer radicals thus formed react with oxygen, forming first hydroperoxide radicals and subsequently hydroperoxide

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