

Figure 1. EPR spectrum of triplet carbene, T ($H_x, H_x, H_y, H_x, H_{dq}$), quintet radical pair, Q ($H_{x,y,z}$), etc., and unidentified doublet radical D generated in the $\lambda \geq 345$ nm photolysis of 9-diazo-10-anthrone powder at 77 K and recorded at 20 K. The klystron frequency was 9.368, GHz. The error bars indicate the range of reproduced resonance lines which have been positively assigned.

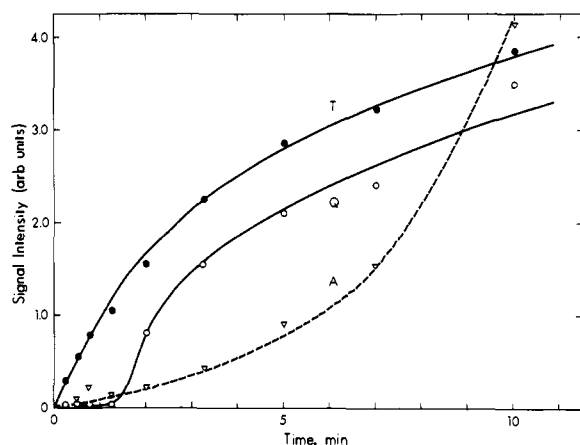


Figure 2. Time dependence of the ESR signals during photolysis of 9-diazo-10-anthrone powder at 77 K. T = **3a**; Q = **Q2**; A = doublet radical.

microwave power intensity it is possible to clearly distinguish between these two different spectra, as seen from Figure 3.

Exposure time studies (Figure 2) showed that the ESR absorption of **3a** was linear with time, while the intensity of the quintet spectrum featured some induction period in the initial stage. This result is similar to that of the azibenzil case and is consistent with the postulate that the quintet species is formed from the interaction of two triplets of **3a**.

All these ESR signals are stable for hours at 77 K, but when the photolysate is warmed to 160 K, both **3a** and the quintet signals fade slowly. The quintet decays somewhat faster than **3a**. Conversion of the quintet spectrum to a new triplet spectrum which was observed in the case of azibenzil¹ did not occur here. A weak signal corresponding to a $\Delta m = 2$ transition of a triplet having small zero field parameters ($D^* = (D^2 + E^2)^{1/2} \sim 0.020$ cm⁻¹, from H_{\min}) was observed, while the $\Delta m = 1$ transition was obscured by the superimposed strong absorption of the doublet radical. However, this H_{\min} seems to coexist with one of the quintet signals before annealing. The origin of this triplet has not been established.

The apparent signal growth which was observed in the azibenzil case¹ in the dark immediately after cessation of irradiation was not observed in the present case. Photolysis of **2a** in an ethanol glass matrix produced only **3a** and the doublet radical.

In summary, it may be stated that the quintet state radical pair formed between two triplet carbenes from the photolysis of 9-diazo-10-anthrone reported here provides an additional example of a quintet state radical pair to the one reported earlier, from

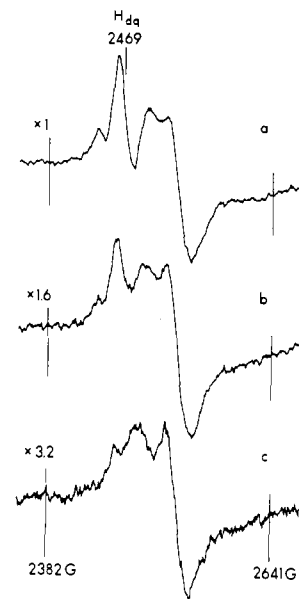


Figure 3. Microwave power dependence of the ESR spectra of the quintet and the doublet quantum transition of **3a** (H_{dq}) at 14 K. Attenuation: (a) 7, (b) 12, and (c) 20 dB at a klystron frequency of 9.371 GHz.

the interaction of two triplet benzoylphenylmethylenes.

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An Efficient, High Conversion Photoinduced Emulsion Polymerization. Magnetic Field Effects on Polymerization Efficiency and Polymer Molecular Weight

Sir:

An emulsion polymerization (EP) typically involves four fundamental ingredients: (1) an aqueous dispersion medium, (2) dispersed droplets of monomer, (3) a micelle-generating detergent,

and (4) an initiator.¹ EP is commonly employed to produce high molecular weight polymers at relatively rapid rates. The conventional mechanism² of emulsion polymerization, the Smith-Ewart (S-E)³ theory, considers three general stages of EP: (1) an initial stage in which the loci of initiation of polymerization are micelles swollen with monomer molecules, during which dispersed monomer droplets serve as a reservoir of monomer molecules, and "nuclei" of growing polymer particles are produced in micelles, and toward the end of which (10–20% conversion of monomer) the number and size of growing polymer particles increase and the number of micelles decrease because detergent molecules become preferentially adsorbed on growing polymer particles which swell with monomer that is available from the dispersed droplet reservoir; (2) a second stage during which the major growth of polymer occurs as the volume of monomer swollen polymer particles increases and the volume of monomer reservoir decreases and also during which the loci of polymerization are considered to be exclusively the polymer particles; (3) a final stage during which the monomer disappears completely and the unreacted monomer exists only in swollen polymer particles.

The S-E theory provides a satisfactory framework for interpretation of the exceptional features of EP: simultaneous achievement of high molecular weight polymer and high polymerization rate result from the generation of a large number of isolated microscopic reaction vessels (in stage 1) that allow for uninterrupted propagation of polymerization in the absence of chain transfer or termination. The use of water-soluble initiators allows termination to be minimized since initiation will involve a single radical which is delivered from the aqueous phase to a monomer swollen micelle or monomer swollen polymer particle. "Oil-soluble" initiators are commonly ineffective in EP,² as is to be expected, because such initiators will produce pairs of radicals in the polymerization loci, thereby favoring termination before substantial polymer growth can occur.

If one of the partners of a radical pair produced by an oil-soluble initiator could be induced to escape into the aqueous phase at a rate that is faster than either monomer is attacked or at which radical combination occurs, a situation would arise that is analogous to that achievable with water-soluble initiators. The production of triplet radical pairs is clearly one method to produce long-lived radical pairs.⁴ Furthermore, application of relatively weak magnetic fields (<500 G) has been shown to substantially enhance the efficiency of escape of radicals from radical pairs produced in micellar aggregates.⁵ Accordingly, we report an investigation of (1) the EP of styrene that is induced by photolysis of ketones known to produce triplet radical pairs and (2) the influence of the application of weak magnetic fields on the rate of EP and molecular weight of the product.

Typically, polymerization was affected by irradiating (313 nm isolated with K₂CrO₄ filter Pyrex vessel, 450-W medium-pressure cylindrical immersion-type Hg lamp) an aqueous system containing dispersed styrene (Sty), sodium dodecyl sulfate (SDS), and initiator. In these experiments, the solution was stirred vigorously with a magnetic stirring bar that was driven by a magnetic stirrer. The magnetic field generated in the proximity of the sample by the bar and the stirring magnet was of the order of 150 G. Polymer was precipitated by addition of reacted solutions to methanol. The yield of dried polymer and its average molecular weight were then determined (Table I). From the data it is seen that photochemical initiation of polymerization by dibenzyl ketone (DBK) and benzoin (BZ) (a) can be carried to conversions that are comparable to those achieved by employing conventional aqueous soluble thermal initiators and (b) can achieve

Table I. Molecular Weight and Yield of Emulsion Polymer

initiator ^a	M_r ^d	% yield ^e	polymerization time, h
DBK	4.6×10^6	82	6
DBK ^b	4.6×10^4	5	20
BZ	5.5×10^6	75	4
BZ ^b	6.0×10^4	4	4
KGA	8.8×10^6	80	8
KGA ^b	1.3×10^6	1	8
SP ^c	1.3×10^6	85	10

^a Except where specified, the typical initial solution contained 1–2% SDS, 0.05–0.06% initiator, 2–3 mL of styrene, and 5–6 mL of water. ^b Conditions as for (a) except that no SDS is present. ^c The initial solution contains 1% SDS, 0.067% SP, and 2 mL of styrene in 12 mL of water. The polymerization was carried out at 65 °C. ^d The molecular weight was computed by measuring intrinsic viscosity with capillary viscometer by Huggins and Kraemer (Huggins, M. L. *J. Am. Chem. Soc.* 1942, 64, 2716. Kraemer, E. O. *Ind. Eng. Chem.* 1938, 30, 1200). The conversion of intrinsic viscosity to molecular weight follows the equation: $[\eta] = KM^a$, where K and a are obtained from the literature: Breitenbach, J. W.; Gabler, H.; Olaj, O. F. *Makromol. Chem.* 1964, 81, 32. ^e Based on the initial amount of styrene monomer. The yield corresponds to the weight of polymer that is precipitated by addition of the reacted emulsion solution.

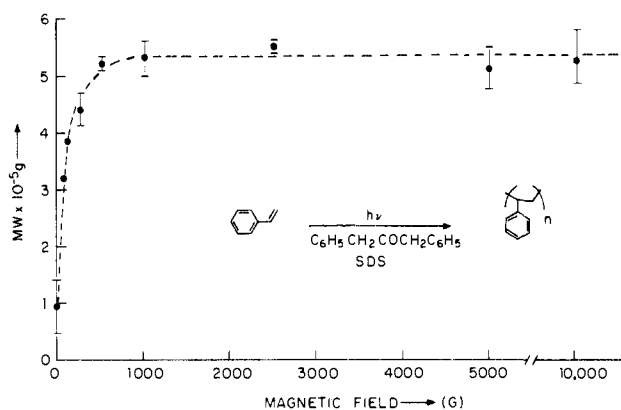


Figure 1. Magnetic field dependence of the average molecular weight of polystyrene produced by emulsion polymerization photoinitiated by dibenzyl ketone.

molecular weights ($>5 \times 10^6$ g) comparable or higher than those achieved by employing conventional aqueous soluble thermal initiators.⁶

With DBK as photoinitiator, we next determined the average polymer molecular weight (M_r) and the rate of polymerization as a function of magnetic field strength.⁷ A sample tube was placed between the poles of an Alpha Model 4600 constant electromagnet and the magnetic field at the sample was varied from ~ 0 to 10 000 G. The M_r determinations are shown in Figure 1. It is noted that the M_r of the isolated polymer increases by a factor of five with increasing field strength. The yield of polymer for comparable periods of irradiation also varies with magnetic field strength in a manner qualitatively the same as the molecular weight.⁸ It was found that neither the M_r of polymer produced

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(2) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; p 203 ff.

(3) Smith, W. V.; Ewart, R. W. *J. Chem. Phys.* 1948, 16, 592.

(4) Turro, N. J. "Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

(5) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Weed, G. C.; Kraeutler, B. *J. Am. Chem. Soc.* 1980, 102, 4843.

(6) The intensity of photoexcitation was found to influence both the rate of conversion to polymer and the polymer-average molecular weight. Higher intensities produce lower average molecular weights. For example, when photoexcitation is provided by a focused high-pressure mercury lamp, molecular weights of the order of $\sim 5 \times 10^5$ are achieved when the system is agitated as described above with a magnetic stirrer. Remarkably, when the agitation method involved an air-driven stirrer, the rate of conversion of polymer and the average molecular weight of the polymer decreased dramatically!

(7) These experiments employed solutions containing 4% SDS, 0.047% DBK, and 1 mL of styrene in 5 mL of water. The solution was placed in a 2-cm-diameter Pyrex tube which was stirred with an air-driven glass stirrer. The excitation light (313 nm as above, provided by a high-pressure Hg lamp operated at ~ 450 W) was focused onto a ~ 1.5 -cm-diameter area of the Pyrex Tube.

by aqueous soluble photoinitiator β -ketoglutaric acid (KGA) nor the aqueous thermal initiator sodium persulfate (SP) varied with application of an external magnetic field. Thus, the effect is unique to oil-soluble photoinitiators.

What is the mechanistic basis of the magnetic field effect and at what stage(s) of the polymerization does it operate? From our recent work⁵ on cage reactions of triplet radical pairs in micelles, we postulate that it is the Zeeman splitting of the T_{\pm} triplet levels from the singlet level which causes the magnetic field effect by decreasing $T_{\pm} \rightarrow S$ intersystem crossing and thereby allows for an increase in the efficiency of radical escape. A more efficient escape of radicals simultaneously allows a more efficient initiation of polymerization and formation of a greater number of polymer particles (by reducing the extent of radical pair combination in micelles), a more efficient overall initiation (by escaping radicals which enter other micelles), and a less efficient termination (by inhibiting the extent of combination of propagating radicals and initiator radicals). This postulate is consistent with the relatively low magnetic fields needed to influence polymerization. Furthermore, the efficiency of $C_6H_5^{13}CH_2CO^{13}CH_2C_6H_5$ (DBK- ^{13}C)⁹ as a photoinitiator is significantly less than that of DBK. For example,¹⁰ under comparable conditions DBK as initiator produces a 52% yield of polymer ($M_r = 4.0 \times 10^6$) in 5 h, whereas DBK- ^{13}C as initiator produces a 13% yield of polymer ($M_r = 1.4 \times 10^6$) for the same time period. We interpret this to mean that recombination of $C_6H_5^{13}CH_2 \cdot ^{13}CH_2C_6H_5$ radical pairs in micelles is more efficient than that of $C_6H_5^{12}CH_2 \cdot ^{12}CH_2C_6H_5$ radical pairs. Finally, the efficiency of EP with 4,4'-di-*tert*-butyldibenzyl ketone (DTB) is drastically reduced relative to DBK. For example,¹¹ under comparable conditions, DBK as initiator produces a 68% yield of polymer ($M_r = 3.9 \times 10^6$) in 27 h, whereas DTB as initiator produces a 16% yield of polymer ($M_r = 1.0 \times 10^6$) for the same time period. We interpret this to mean that the more hydrophobic 4-*tert*-butylbenzyl radicals cannot escape from micelles as efficiently as benzyl radicals. The further findings that there are no magnetic field effects on the EP of styrene with water-soluble initiators (SP and KGA) or with oil-soluble initiators that thermolyze to produce micellized singlet radical pairs [azobis(isobutyronitrile) and dibenzoyl peroxide] lend support to the conclusion that micellized triplet radical pairs are required for the observation of magnetic field effects.

Experiments were run in order to establish which stage of polymerization was most sensitive to magnetic field effects. Experiments were conducted under three sets of conditions: (1) photoinitiated EP was run to ~20% conversion in the earth's field for ~1.5 h and then for a comparable period of time at 1000 G; (2) photoinitiated EP was run to ~20% conversion at 1000 G for ~40 min and then for a comparable period of time in the earth's field; (3) photoinitiated EP was run to 20% conversion in either the earth's field or at 1000 G and then the system was allowed to stand in the dark for ~1 h. It was found that the initial stage determined completely the M_r characteristics of the product and that no reaction occurs after the first stage in the dark.

In summary, EP of styrene, photoinduced by an oil-soluble initiator, can proceed to high conversions at convenient rates and produce a polymer of M_r comparable to that achievable in conventional EP by employing a water-soluble initiator. Weak magnetic fields have a significant effect on the EP of styrene only

when oil-soluble initiators are employed.¹² The magnetic field effects appear to operate during the early (micellar) stage of polymerization and to originate from Zeeman inhibition of triplet radical coupling within micelles, which leads to the formation of a larger amount of growing polymer particles and hence to a higher M_r and polymerization rate.

Acknowledgment. We thank the Air Force Office of Scientific Research and the National Science Foundation for their generous support of this work.

(12) Reports of magnetic field effects on solid-state radiation-induced polymerizations have been reported by Mori et al. (Mori, K.; Tabata, Y.; Oshima, K. *Kogyo Kagaku Zasshi* 1970, 73, 1215; *Ibid.* 1970, 73, 815).

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Activation of Methane with Photoexcited Metal Atoms

Sir:

The activation of inert bonds with transition metals has been recognized as an important goal.¹ Recent reports describing the oxidative insertion of diiron into a carbon-hydrogen bond of methane² and of zirconium atoms into the carbon-carbon or carbon-hydrogen bonds of isoalkanes³ prompt us to report some of our results on the reactions of photoexcited metal atoms with methane.

Spectrum A (Figure 1) indicates that no reaction occurs between iron atoms⁴ and methane at 15 K.⁵ Irradiation with $\lambda < 360$ nm causes a new set of peaks at 1653.4, 1153.4, 548.8, 545.9, and 521.1 cm^{-1} to appear as shown in spectrum B. The isotopic shifts observed in spectra C and D indicate that the 521.1- and 1653.1 cm^{-1} peaks can be assigned to the iron-carbon and iron-hydrogen stretching modes, respectively, and suggest that oxidative cleavage of a carbon-hydrogen bond has occurred to yield CH_3FeH (1). The other peaks can be assigned to the hydrogen modes of the methyl group.⁶

Wavelength-dependent photolysis studies indicate that reaction is caused by absorption of the metal atom rather than the metal dimer. Thus, the iron-methane matrix was first irradiated with light which could only photoexcite the assigned⁷ electronic transition of the metal dimer; however, the photoinduced reaction was observed when light was present in the region where the free metal atom is known to absorb.

Similar results were obtained when other metals were codeposited with methane and irradiated. Thus, Mn, Co, Cu, Zn, Ag, and Au all reacted with methane to give insertion products analogous to 1, whereas Ca, Ti, Cr, and Ni failed to yield insertion products. The infrared absorption frequencies of these products are presented in Table I.

(1) J. P. Collman et al., N.T.I.S. Bulletin PB-240 177, "Workshop on Fundamental Research in Homogeneous Catalysis as Related to U.S. Energy Problems," held at Stanford University, Stanford, CA, Dec 4-6, 1974.

(2) P. H. Barrett, M. Pasternak, and R. G. Pearson, *J. Am. Chem. Soc.*, **101**, 222 (1979).

(3) R. J. Remick, T. A. Asunta, and P. S. Skell, *J. Am. Chem. Soc.*, **101**, 1320 (1979); see also S. C. Davis and K. J. Klabunde, *ibid.* **100**, 5973 (1978).

(4) Iron atom concentrations from 0.1% to 1% were used.

(5) The apparatus has been described previously: NBS Spec. Publ. (U.S.) 561, Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases held at NBS, Gaithersburg, MD, Sept 18-22, 1978. Concentrations were measured with a quartz crystal oscillator mounted on the 15 K copper block.

(6) The peaks reported by Barrett, Pasternak, and Pearson² were not observed.

(7) T. C. DeVore, A. Ewing, H. F. Franzen, and V. Calder, *Chem. Phys. Lett.*, **35**, 78 (1975).

(8) The oxygen was removed by bubbling argon through the solution for at least 30 min at room temperature. Nevertheless, residual oxygen appears to cause the polymerization to have induction periods which vary somewhat from sample to sample. As a result, the yield of polymer was not reproducible to better than a 20% error for short polymerization periods (≤ 3 h). Generally, for the magnetic field studies, the polymerization was carried out for longer than 12 h. At this stage, the conversion of polymerization is about 90%. It was found that the molecular weight is independent on the conversion range 20%-90%. The available data for the conversion of polymerizations are about 30% and 90% at 0 and 250 G, respectively, for 3-h irradiation.

(9) DBK- ^{13}C contains 90% ^{13}C at both the 2 and 2' carbon atoms.

(10) Initial reaction concentrations: SDS = 0.05, DBK = 0.0013, DBK- ^{13}C = 0.0015 M.

(11) Initial reaction concentrations: SDS = 0.05, DBK = 0.0005, DTB = 0.0008 M. The low solubility of DTB requires lower initiator concentrations and forces longer reaction times.