provide substantial evidence that neither the slow nor fast decay involves benzyl radicals that escape from HDTCl micelles.[14]

Only recently have time-resolved magnetic field effects on the dynamics of radical pairs been measured.[15-18] Our results confirm many of the conclusions concerning the behavior of radical pairs in micelles that were proposed on the basis of steady state measurements.[19] It is noteworthy that the time scales for geminate reactions of radical pairs in micelles are now confirmed, by direct spectroscopic measurement, to be several orders of magnitude greater than the time scale for analogous processes in homogeneous solution.

In summary, the laser flash excitation of DBK in HDTCl solution produces geminate triplet radical pairs in micelle aggregates. These geminate pairs decay by two major pathways in the time domain 50-50 000 ns: ISC of spin-correlated triplet radical pairs followed by combination of singlet radical pairs to form diphenylethane (k_f) and recombination of relaxed geminate radical pairs to form diphenylethane (k_s). The rate of spin correlated ISC is substantially decreased by application of a magnetic field of 400 G and is substantially increased by ^{13}C in the CH_2 groups of the benzyl radicals. The relaxed geminate radical pairs are not sensitive to either magnetic effect. The escape of benzyl radicals from micelles occurs on a longer time scale than that explored in this investigation.

Acknowledgment. We thank the Air Force Office of Scientific Research and the National Science Foundation for their generous support of this research. We also thank Drs. H. Hayashi and S. Nagakura for informing us of their results on the photolysis of DBK in anionic sodium dodecyl sulfate micelles. Dr. Gary Lehr is thanked for his important comments relevant to the interpretation of the data.

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Polymerization of Acetylenes, 1,3-Dienes, and Allyl Halides on Active Uranium Powder

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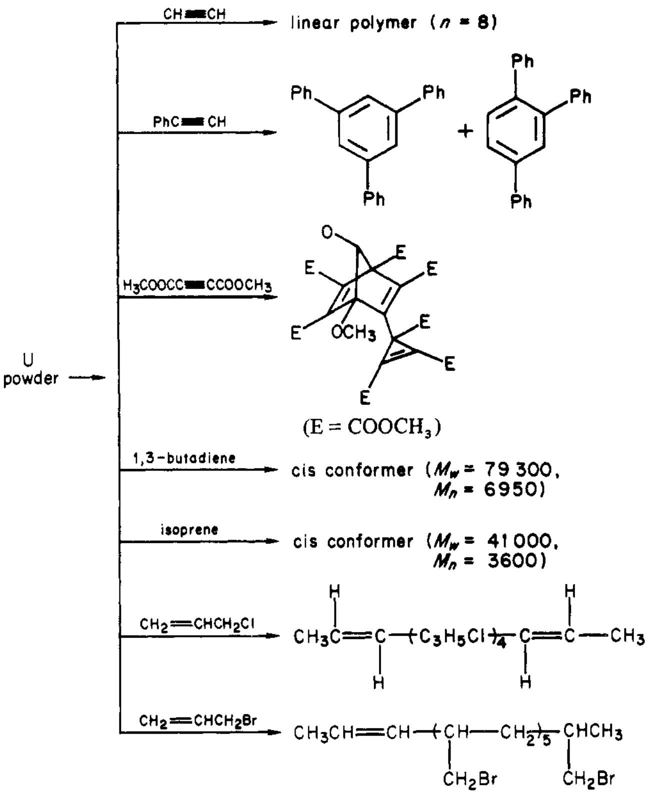
Received November 10, 1980

During the past decade there has been a considerable upsurge of research activity in the chemistry of metal vapors, aiming mainly at the facile syntheses of organometallic complexes and the initiation of a variety of chemical reactions by active metal atoms or cluster.[1] A hitherto unnoticed but related technique of producing large quantities of active uranium metal powders by means of electrolytic amalgamation has recently been shown to provide a simple and energy-saving route to organouranium compounds and other related materials.[2] The higher activity of this uranium powder in comparison with that from other methods is demonstrated by its very high reactivity in the synthesis of uranocene.[3] Other pronounced features of this metal powder have been further revealed in its reactions with various substrates, giving rise to various kinds of hydrocarbons, oligomers, and polymers. The metal powder was repeatedly used for five times, and its catalytic activity remained virtually unchanged.

Scheme I



In this communication we describe the reactions of the uranium powder with acetylenes, 1,3-dienes, and allyl halides at room temperature, which outlines unexpected results as shown in Scheme I. This work demonstrates the first example of an f-block element induced polymerization.

All operations were carried out in an N_2-flushed glove bag or an evacuated system. The starting material, uranium amalgam, was prepared as previously described.[4] The uranium amalgam was washed with dilute HCl, water, and acetone and finally placed in an apparatus designed for the decomposition and removal of mercury at 150 °C and 10^{-4} torr. Liquid organic substrates were then introduced onto the thereby obtained black, fresh uranium powder, whereas the gaseous substrates were cocondensed with benzene on the powder. The reactions of 10 g of uranium powder with dimethyl acetylenedicarboxylate (4 mL), phenyl acetylene (5 mL), and acetylene (4 mmol) gave different kinds of polymers. Kauer et al.[5] and Lacount et al.[6] heated dialkyl ethers of acetylenedicarboxylic acid at 85 °C for 10 days and at 120 °C for several hrs, respectively, to obtain the tetramer tetramethyl 4-methoxy-5-[1,2,3-tris(methoxycarbonyl)-2-cyclopentenyl]-1-oxabicyclo[2.2.1]hepta-2,5-diene-1,2,3,6-tetracarboxylate, whereas in the presence of our uranium catalyst the reaction proceeds at room temperature to give 70% yield in only 2 h. The reaction mixture was filtered, and unreacted substrate was pumped out.

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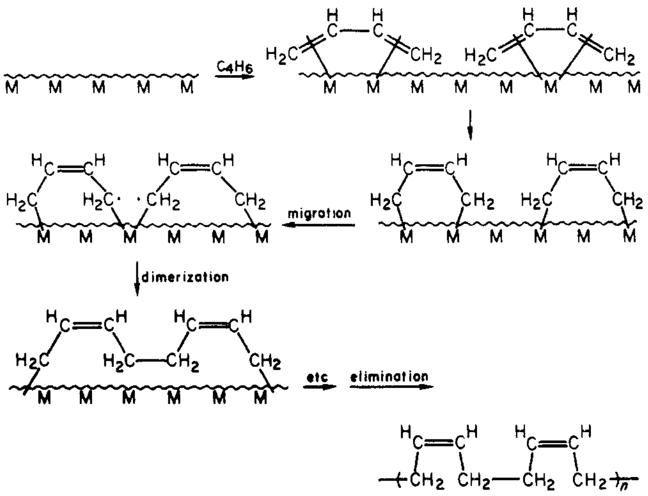
Scheme II



The solid was recrystallized with absolute alcohol and was found to be a tetramer.[7] The reaction of phenylacetylene proceeded even faster; the reaction mixture turned from yellow to brown within 10 min and consumed 60% of the substrate. The product which was separated with a silica gel column was found to consist of 1,2,4-triphenylbenzene (90%) and 1,3,5-triphenylbenzene (5%), respectively.[8] The tetramer and the trimers of the above products were characterized by IR, mass, and ^{1}H NMR spectra, which were all in agreement with the published data.[7-10] Because of its relatively low yield of only 3%, the product from the reaction of acetylene could not be isolated in a weighable amount; however, spectral data indicate it to be a linear polymer.[11] The activation of acetylene shown in this work cannot be interpreted in terms of existing theories of homogeneous catalysis. However, it is possible that the reaction forms the final products via biradical intermediates,[12-14] which are formed at the outset and combine successively with mobile acetylene molecules to form a linear polymer. The substituted acetylenes gave cyclooligomers, possibly because the bulkiness of the substituting group allowed the chain to bend toward the uranium surface with the consequence of cyclization. The degree of polymerization was found to depend on the substituting groups, viz., acetylene ($n > 8$) > dimethyl acetylenedicarboxylate ($n = 4$) > phenylacetylene ($n = 3$) > diphenylacetylene ($n = 1$).

Four hundred milliliters of benzene and 1,3-butadiene (1 atm) were cocondensed on the metal powder; 80% of the butadiene was consumed after 4 h at 70 °C. Both IR and ^{1}H NMR data were in accordance with the published data of *cis*-1,4-polybutadiene.[15] The composition of the polymer was estimated according to Silas et al.[16] On the basis of IR data, it contained 94% cis, 3% trans, and 3% vinyl polymer. Similarly isoprene (50% consumption) was also polymerized to the cis conformer.[17] The average molecular weight was determined by gel permeation chromatography and found to be $M_r = 79\,300$ and $M_n = 6950$ (for polybutadiene) and $M_m = 41\,000$ and $M_n = 3600$ (for polyisoprene).

The predominance of cis conformers in this work, which is due to an obvious heterogeneous reaction, might be indicative of some resemblance with a homogeneous reaction. In an attempt to obtain some clues about reaction mechanism, NMR techniques were employed. However, no organouranium complex intermediates were observed. Chemisorption on the uranium powder surface might play an important role in this reaction as reported previously.[18] It is improbable that the polymerization could ensue at a single atom on a metal surface; surface chemical reactions are structurally incomplete, because more than one metal atom might be bound to a chemisorbed radical or molecule. One of the plausible mechanisms is shown in Scheme II, which assumes high mobility for molecules or atoms on a surface. Two chemisorbed *cis*-butadiene molecules at nearby sites migrate toward each other to the same or neighboring atoms, which results in dimerization. The process continues until the polymer becomes large enough to block further propagation. The molecular weight distribution was found to spread over a relatively wide range; this might be due to the irregularity both in shape and size of the metal powder.

An excess amount of allyl chloride (50 mL) reacted with 6 g of fresh uranium powder at room temperature for 72 h. The liquid portion of the reaction mixture changed from colorless to green and finally to brown and was checked intermittently by a liquid chromatograph until a steady state had been reached. Eighteen milliliters of unreacted substrate were distilled out, and 6 g of brown viscous fluid were obtained. The products were extracted with cyclohexane and separated with a liquid chromatograph; only the major product was collected in appreciable quantity to allow for the subsequent analyses. This product has been characterized as $C_{18}H_{30}Cl_4$ on the basis of various spectral determinations. Mass spectral data established its molecular composition and molecular weight, which are in agreement with the results of elemental analyses. Elemental analyses are as follows. Anal. Calcd for $C_{18}H_{30}Cl_4$: C, 55.67; H, 7.73, Cl, 36.60. Found: C, 54.03; H, 7.43; Cl, 39.85. Characteristic fragmentation ions occur at *m/e* (assignment in parentheses) 386 ($C_{18}H_{30}Cl_4^+$), 304 ($C_{12}H_{20}Cl_4^+$), 268 ($C_{12}H_{19}Cl_3^+$), 228 ($C_9H_{15}Cl_3^+$), 193 ($C_9H_{15}Cl_2^+$), 178 ($C_8H_{12}Cl_2^+$), 157 ($C_9H_{14}Cl^+$), 152 ($C_6H_{10}Cl_2^+$), 142 ($C_8H_{11}Cl^+$), neglecting the isotopic contributions. Although the infrared spectrum is rather complex, useful information from the structural determination is still obtainable from some absorption bands. Bands at 1630 (w) and 970 (s) are characteristic of *trans*-RHC═CHR′, whereas 1460 (s) and 1380 (m) and 1290 (s), 730 (s), and 660 (s) represent the C–H bond of CH_3C RCH_2Cl, respectively.

The ^{1}H NMR spectrum shows three regional broad peaks centered at 5.2, 3.2, and 1.5 ppm, indicating the presence of HC═CH, CH_2Cl, and CH, respectively. The integrated areas are in the ratio 1:2.6:6.7 as compared with the theoretical ratio 1:2.6:5.9. The ^{13}C NMR spectrum shows 9 different environments for the carbon atoms. The presence of the double bonds at terminal positions could be ruled out for the resonances at 129.76 and 129.27 ppm.[19] Owing to the long chain in this compound,

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[7] 99–101 melting point °C. The IR absorptions (KBr pellet) occur at 3010 (w), 2965 (m), 2860 (w), 1860 (m), 1760–1720 (br s), 1630 (m), 1440 (s), 1335 (s), 1280 (br, s), 1207 (s), 1140 (s), 1062 (s), 1010 (m), 984 (w), 968 (w), 922 (w), 910 (w), 844 (w), 828 (m), 813 (m), 786 (m), 776 (w), 760 (w), 728 (s), 632 (s). The ^{1}H NMR spectrum (acetone-d_6) shows resonances at δ 3.255 (1 H), 3.318 (1 H), 3.385 (1 H), 3.438 (1 H), 3.505 (1 H), 3.528 (1 H), 3.545 (1 H), 3.620 (1 H) ppm. The 12 most intense mass spectral envelopes (70 ev) occur at *m/e* (relative intensity) 568 (30.4), 509 (95.7), 480 (82.6), 464 (90.2), 452 (31.5), 435 (72.8), 406 (34.8), 390 (42.4), 362 (32.6), 239 (100), 103 (50.0), 57 (82.6).

[8] 1,2,4-Triphenylbenzene (mp 121–125 °C): infrared absorptions (KBr pellet) occur at 3060 (m), 3035 (m), 1601 (m), 1580 (w), 1494 (s), 1478 (w), 1445 (m), 1070 (m), 1035 (m), 910 (m), 760 (s), 700 (s), 580 (w), 540 (w). The six most intense mass spectral peaks occur at (70 ev) *m/e* (relative intensity) 306 (100), 288 (72), 307 (27), 289 (18), 291 (15), 305 (14). 1,3,5-Triphenylbenzene (mp 172–175 °C): infrared absorptions (KBr pellet) occur at 3080 (m), 3050 (m), 1598 (s), 1580 (w), 1500 (s), 1480 (w), 1425 (w), 1416 (s), 1080 (m), 1032 (m), 878 (s), 770 (sh), 756 (s), 701 (s), 696 (s), 614 (m), 504 (w). The six most intense mass spectral peaks occur at (70 ev) *m/e* (relative intensity) 306 (100), 307 (26), 289 (7), 302 (4), 228 (4), 303 (4). Both compounds were also characterized qualitatively with liquid chromatography.

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it is rather difficult to determine the structure of the portion in parenthesis for $CH_3CH{=}CH{-}(C_3H_5Cl)_4{-}CH{=}CHCH_3$. Four structures could be derived; however, the mass spectral data indicate one of the structures as 4,6,9,11-tetrachloromethyl-2,12-tetradecadiene.

An excess amount of allyl bromide (60 mL) reacted with 6 g of fresh uranium powder at 25 °C. The liquid chromatogram showed four products with comparable peak heights in a reaction time of 8 h which subsequently merge into a single product after 60 h. unreacted allyl bromide (15 mL) was recovered, and the final product was collected and characterized as $C_{21}H_{36}Br_6$. Although mass spectral data did not give a parent peak, characteristic fragmentation did occur at *m/e* (assignment in parentheses) 360 ($C_9H_{15}Br_3^+$), 320 ($C_{12}H_{18}Br_2^+$), 280 ($C_9H_{14}Br_2^+$), 240 ($C_6H_{10}Br_2^+$), 200 ($C_9H_{13}Br^+$), 160 ($C_6H_9Br^+$), 119 ($C_3H_4Br^+$), 93 (CH_2Br^+), 80 (HBr^+), 79 ($C_6H_9^+$ or Br^+), 67 ($C_5H_7^+$), 57 ($C_4H_9^+$), 55 ($C_4H_7^+$), 43 ($C_3H_7^+$), 41 ($C_3H_5^+$), neglecting the isotopic ions. Elemental analyses are as follows: Anal. Calcd for $C_{21}H_{36}Br_6$: C, 32.81; H, 4.69; Br, 62.50. Found: C, 31.45; H, 4.42; Br, 64.52.

The infrared spectra give characteristic absorptions of *trans*-RHC=CHR′ at 1640 (w) and 1250 (s), CH_2Br at 1250 (s), 650 (m), and 572 (s), and CH_3C at 1440 (s) and 1380 (m). The ^1H NMR spectrum exhibits three regional broad band peaks at 5.21, 3.57, and 1.55, corresponding to HC=CH:CH_2Br:CH, respectively, with the integrated area in the ratio 2:10:22 in comparison with the theoretical ratio of 2:10:22. ^{13}C NMR shows 21 different environments of the carbon atoms. The presence of double bonds at terminal positions might be improbable because of the chemical shifts at 129.48 and 128.75 ppm. Although a fragment corresponding to $C_5H_7Br^+$ was not observed, its presence seems reasonable since the C–Br bond is as easily broken as the C–H bond to give a 40 mass unit difference; however the cleavage of the C–Cl bond is more difficult. Therefore the structure is assumed to be similar to the allyl chloride system—4,6,8,10,12-pentakisbromomethyl)-2-octadecene.

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Reaction of Primary Amines with the Dichlorocarbene Complex of Iron(II) Tetraphenylporphyrin [$Fe^{II}TPP(CCl_2)$]

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Received February 12, 1981

The hepatotoxicity of $CHCl_3$ has been related to the irreversible binding of its metabolites to cellular macromolecules.[1] Recent evidence supports the view the $CHCl_3$ hepatic metabolism is at least partly cytochrome P-450 dependent[2] and involves the formation of a dichlorocarbene intermediate.[3-6] Mansuy and collaborators[7,8] have shown that various polyhalogenated compounds form stable iron(II) porphyrin halocarbenes under reducing conditions and the carbene moiety of $Fe^{II}TPP(CCl_2)$ to be susceptible to aminolysis.[9] Herein we report the results of a kinetic investigation which establishes two alternate mechanisms for the reaction of primary amines with $Fe^{II}TPP(CCl_2)$.[10]

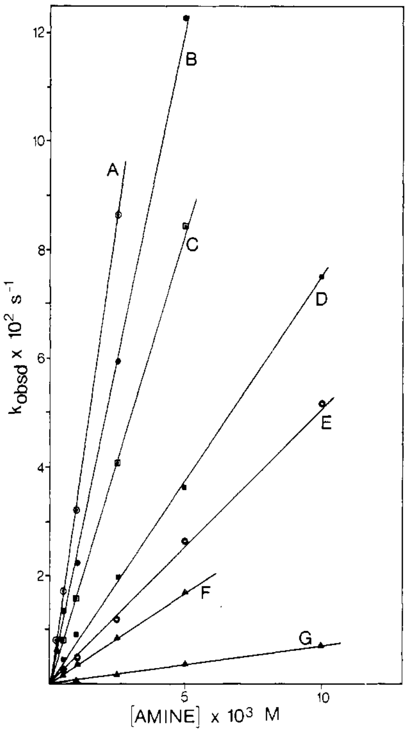

Figure 1. Plot of the pseudo-first-order rate constants (k_{obsd}, s^{-1}) at 30 °C vs. amine concentration for the reaction of representative amines with the corresponding amine complex of $Fe^{II}TPP(CCl_2)$. (A) *n*-Butylamine in toluene; (B) benzylamine in toluene; (C) *n*-butylamine in dioxane; (D) cyclohexylamine in toluene; (E) *n*-butylamine in *tert*-butyl alcohol; (F) isopropylamine in toluene; (g) *o*-phenylenediamine in toluene.

We have found that primary amines react with $Fe^{II}TPP(CCl_2)$ to provide the axial coordinated complex $RNH_2Fe^{II}TPP(CCl_2)$ which then reacts with additional primary amine. Sterically hindered or weakly basic primary amines provide as products both the amine–isonitrile complex [$RNH_2Fe(II)TPP(C{=}NR)$][9,11] and the diamino complex [$(RNH_2)_2Fe^{II}TPP$], while the remaining primary amines yield the amine–isonitrile complex as the overwhelming product. Thus, the reaction of $Fe^{II}TPP(CCl_2)$ [λ_{max} 408 nm (ϵ 2 × 10^5 M^{-1} cm^{-1}) and 524 (1.5 × 10^4)] with 1 equiv of *n*-$BuNH_2$ in toluene (30 °C) provides (*n*-$BuNH_2$)$Fe^{II}TPP$

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(10) Solvents and amines were dried by refluxinng over CaH_2, distilled under N_2, and further degassed by purging with N_2 or by several cycles of freeze–vacuum–thaw. Inert atmosphere techniques were employed *throughout* the study. Tetraphenylporphyrin (Aldrich) was converted to $Fe^{III}TPPCl$ and separated from $O[Fe^{III}TPP]_2$ by chromatography over dry alumina (activity grade I) with anhydrous chloroform. $Fe^{II}TPP(CCl_2)$ was prepared by addition of 1 mL CCl_4 and 500 mg of iron powder (see ref 7) to 50 mg $Fe^{III}TPPCl$ in 50 mL of CH_2Cl_2/CH_3OH (9:1) and shaking it by hand for ~30 min. It is important to activate the iron powder by washing with glacial acetic acid, dry CH_3OH, and CH_2Cl_2 under a dry inert atmosphere. After filtration, the pink solution was reduced in volume by purging with N_2 and the residue recrystallized three times from CH_2Cl_2 and CH_3OH.

The product $Fe^{II}TPP(CCl_2)$ was identified by comparison of IR, visible, and H NMR spectra to the literature values.[7] That the dichlorocarbene complex was truly in hand was further established by showing that 1,1-dichloronorcarane was formed when oxygen was passed through a toluene solution 1 M in cyclohexene containing ~20 mg of $Fe^{II}TPP(CCl_2)$. 1,1-Dichloronorcarane product was detected via GC (Apiezone Carbowax) and shown by this means to be identical with an authentic sample (Doering, W. von E.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1954**, *76*, 6162).

(11) With *n*-$BuNH_2$ the isonitrile complex was shown to be identical with the product of Mansuy et al. by comparison of IR (ν_{CN} 2135 cm^{-1}) as well as visible spectra (lit.[9]).

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