Table I. Preparation of Hydrocarbons (C_1–C_5) over Various Phthalocyanine–Sodium EDA Complexes and Graphite–Sodium Complex

Acceptor (g)	Donor (g)	H_2, cm	CO, cm	Temp, °C	Total amt of hydrocarbons, ml	%[a] C_1	C_2	C_3	C_4	C_5
Fe–Pc	Na	45	15	240	18	4	89	5	2	0
(0.2)	(0.5)	45	15	170	1.9	38	59	3	1	0
Co–Pc	Na	45	15	240	11	6	91	3	1	0
(0.2)	(0.5)	45	15	180	1.8	58	38	4	0	0
Pt–Pc	Na	46	12	220	10.2	2	82	9	6	1
(0.2)	(0.5)									
H_2–Pc	Na	45	15	240	2.4	10	84	6	0	0
(0.2)	(0.5)									
Graphite	Na	40	10	300	1.4	2	74	22	2	0
(5)	(2)									

[a] C_1, methane; C_2, ethylene + ethane; C_3, propylene + propane; C_4, 1-butene + *cis*-2-butene + *trans*-2-butene + butane; C_5, pentane, 1-pentene.

brought into contact with sodium or potassium, resulting in the formation of the electron donor–acceptor (EDA) complexes. It has been also demonstrated that the catalytic formation of ammonia from N_2 and H_2 takes place appreciably over the transition metal–Pc (phthalocyanine) or graphite complexes with alkali metals (Na or K) under mild conditions.[3]

The deeply colored stable EDA complex films were prepared by the successive evaporation of each of the phthalocyanines (Fe, Co, Ni, Mo, Pt, and H_2) and sodium on the wall of the reaction vessel similarly as described previously.[1-3] The graphite–Na (or K) complex was also obtained in the reaction between graphite powder and distilled sodium or potassium. Carbon monoxide (20 cm of Hg) was sorbed to a considerable extent on each EDA complex film in the temperature range between 25 and 200°, but the desorption proceeded very slowly even at higher temperatures such as 200°. When hydrogen (20 cm of Hg) was admitted at 170° onto the complex films which preadsorbed CO, a considerable amount of hydrogen was taken up[4] and a mixture of hydrocarbons such as ethane, ethylene, and propane was detected by gas chromatography in a closed circulating reaction system (140 ml).

A mixture of CO and H_2 with various relative molar ratios reacted over each phthalocyanine EDA complex film with excess sodium in the temperature range between 25 and 260°. Various kinds of hydrocarbons (C_1–C_5) were formed at temperatures above 90° in 20 hr. The amount of hydrocarbons and the distribution of the products (in the steady state) are shown in Table I. It was found that when the portion of CO in the CO–H_2 mixture was increased, the yield of the hydrocarbons decreased markedly, probably because CO retarded hydrogen activation by the complex films.

It was interesting to note that a small amount of methanol and ethanol and a trace of CO_2 were detected in the product at lower temperatures such as 120° under CO-rich conditions over Fe–, Mo–, and Pt–Pc complex films. A trace of water was obtained in each run even at higher temperatures. The reactivity of the complexes did not change appreciably in several runs. The amount of higher hydrocarbons (C_3–C_5) increased considerably at 240° over the Fe–Pc complex film when the content of CO in a mixture gas was increased. It was also found that the amount of methane increased in the reaction at lower temperatures under hydrogen-rich conditions. The product distributions were not so appreciably dependent upon the sorts of the central metal ions of each phthalocyanine except that methane was produced to a greater extent over the Fe–, Co–, or Mo–Pc EDA complex than the other complex films under similar reaction conditions.

Similar hydrocarbons were also formed when a mixture of CO and H_2 was admitted to the graphite–Na (or K) complex in the temperature range between 200 and 350°.

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(3) M. Sudo, M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, submitted for publication.

(4) CO and H_2 adsorptions took place negligibly over each phthalocyanine or sodium film alone in the temperature range studied.

Temperature Dependence of the Reaction Yields from Recoil Tritium Reactions. I. Energetics of Tritium Atom Addition to Olefins

Sir:

Chemical processes initiated by very high kinetic energy atoms have correspondingly lesser requirements for initial thermal excitation energy in the struck molecule, and a lack of dependence of reaction rate upon temperature is frequently cited as proof of the "hot" atom character of the reactions.[1,2] Earlier searches for a temperature dependence in recoil tritium reactions have either failed to detect any change in yield *vs.* temperature,[3,4] or else have simultaneously involved both phase and temperature changes.[5,6] We have now observed and measured both the temperature and pressure effects on the decomposition

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(1) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

(2) F. Schmidt-Bleek and F. S. Rowland, *Angew. Chem. Intern. Ed. Engl.*, **3**, 769 (1964).

(3) M. A. El-Sayed, P. Estrup, and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

(4) W. J. Hoff, Jr. and F. S. Rowland, *J. Am. Chem. Soc.*, **79**, 4867 (1957).

(5) E. K. C. Lee and F. S. Rowland, *J. Inorg. Nucl. Chem.*, **25**, 133 (1963).

(6) B. G. Dzantiev and A. P. Schvedchikov, "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna, 1965, p 87.

of excited *sec*-butyl radicals, as formed by recoil tritium addition to 1-butene or *cis*-2-butene. Evaluation of these changes indicates that about three-fourths of such additions to olefins are initiated by tritium atoms with kinetic energies in the range from 3 eV to thermal energies.

The reaction sequence is illustrated for *cis*-2-butene in eq 1–3; substitution of T for H in the parent molecule also occurs as in (4). The relative yields of $CH_3CH{=}CHT$ from (3) and the labeled parent molecule from (4)

$$T^* + CH_3CH{=}CHCH_3 \rightarrow CH_3CHCHTCH_3^* \quad (1)$$

$$CH_3CHCHTCH_3^* + M \rightarrow CH_3CHCHTCH_3 + M \quad (2)$$

$$CH_3CHCHTCH_3^* \rightarrow CH_3CH{=}CHT + CH_3 \quad (3)$$

$$T^* + RH \rightarrow RT^* + H \quad (4)$$

have been measured at 24 and 125° over a range of pressures from 3 to 76 cm. Similar observations were made concerning the terminal addition of T* to 1-butene, with the results shown in Figure 1. The ratio of the yield of propylene-*t* to that of the labeled parent molecule is higher at the higher temperature by 1.07 ± 0.02 at 5 cm, and 1.04 ± 0.01 at 76 cm for 1-butene experiments, with quite similar results for *cis*-2-butene. Decomposition by (3) accounts for 25–40% of the *sec*-butyl radicals from (1). At each temperature, the yield of propylene-*t* varies more than 30% with a 15-fold change in pressure.

Comparison of experimental results with the extensive data available from thermal H and D reactions with these olefins permits an estimate of the distribution of tritium atom energies involved in the addition reaction.[7–9] Approximately 50% of the tritium atoms adding to the olefins have less than 0.4 eV kinetic energy and are detected as $n\text{-}C_4H_9T$ following the reaction of stabilized $CH_3\dot{C}HCHTCH_3$ with H_2S scavenger. Decomposition of radicals from thermal addition contributes to the observed temperature effect, but the major source of this variation lies with more highly excited radicals formed by reactions of above-thermal-energy tritium atoms. Approximately one-fourth of the addition reactions in (1) have sufficient excitation energy always to decompose in our experiments, corresponding to $\geqslant 3$ eV kinetic energy for the T atom. The tritium kinetic energies for addition reactions are generally much lower than for the substitution of T for H in $c\text{-}C_4H_8$, CH_4, or CH_3NC,[10–12] indicating that a large fraction of these addition reactions occur at energies below the energy threshold for the direct substitution reactions.

Detailed evaluation of the 1-butene system indicates that addition to the terminal position is favored by a factor of 2 or 3. Addition below 1 eV strongly favors the terminal position, as expected from thermal studies, while the higher energy addition proceeds at both positions more or less equally, as postulated by Urch and Wolfgang.[13]

While we are here reporting a temperature dependence of yield for recoil tritium reaction products, we wish to emphasize that our explanation of this observed effect has been made entirely in terms of the temperature effect on the *secondary* decomposition reaction, and not upon the primary reaction itself. Indeed, our treatment implicitly assumes that the primary process occurs in essentially identical manner with groups of molecules at 24 and 125°, with an energy contribution from the hot reaction that is independent of the detailed internal energy of the struck molecule.

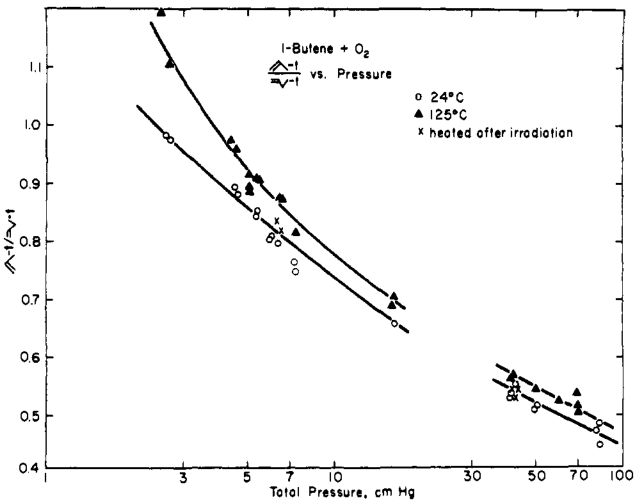

Figure 1.

The experimental procedures are quite routine,[1,2] with the exception of irradiation in thermostated temperature baths at the two temperatures. Samples irradiated at 24°, and subsequently heated to 125° for a time equivalent to that of the irradiation, gave identical results to the standard 24° samples, thereby eliminating the possibility of some temperature-catalyzed alteration of the product distribution.

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[7] Our most detailed quantitative calculations have assumed that a small part of the temperature dependence is contributed by the slightly greater decomposition of RT* at higher temperatures.

[8] B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959).

[9] B. S. Rabinovitch, R. F. Kubin, and R. E. Harrington, *ibid.*, **38**, 1692 (1963).

[10] E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 897 (1963).

[11] Y. N. Tang and F. S. Rowland, *J. Phys. Chem.*, **72**, 707 (1968).

[12] C. T. Ting and F. S. Rowland, *ibid.*, **72**, 763 (1968).

[13] D. Urch and R. Wolfgang, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, 1961, p 99.

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Kinetic Evidence for the Existence of Free Bis(phenylthio)methylene in Solution

Sir:

From a variety of preparative results[1] we concluded[2] some time ago that carbenoid A[3] is in equilibrium with bis(phenylthio)methylene (B) in THF solution. Since the classical work of Hine,[4] who proved that in aqueous

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[1] D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, 6, 443 (1967).

[2] Independently Professor Arens and his coworkers made the same proposal from some observations of the alkylation of A: G. A. Wildschut, H. J. T. Bos, L. Brandsma, and J. F. Arens, *Monatsh. Chem.*, **98**, 1043 (1967).

[3] D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **6**, 442 (1967).

[4] J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.