

Fig. 1.—Plot of line width vs. formation constant for sodium complexes.

Recently, we devised a potentiometric method for the study of weak alkali metal complexes based on the properties of cation-sensitive glass electrodes.^{2,3} Using this technique, seven of the complexes considered by Jardetzky and Wertz have been examined with the objective of determining their formation constants in aqueous media. The results are summarized in Table I.

TABLE I
FORMATION CONSTANTS OF SODIUM COMPLEXES

Complexing agent	pH ^a	K _f
Pyruvic acid	8.45	2.7 ± 0.1
Malic acid	8.38	1.9 ± 0.1
Lactic acid	8.43	1.1 ± 0.1
<i>m</i> -Hydroxybenzoic acid	8.45	0.81 ± 0.1
<i>o</i> -Hydroxybenzoic acid	8.45	0.78 ± 0.1
<i>l</i> -Leucine	8.45	0.3 ± 0.1
<i>dl</i> - α -Alanine	8.48	0.2 ± 0.1

^a pH and ionic strength were controlled with tris(hydroxymethyl)aminomethane-hydrochloric acid buffer mixtures.

The resulting formation constant values are plotted vs. the Jardetzky-Wertz line widths (taken relative to 3 M sodium chloride) in Fig. 1. Considering the relative uncertainties in both formation constant and line width (± 0.05) values, a surprisingly good straight line is obtained. In view of the fact that this plot meets the additional requirement that the absorption line not be broadened when no complexing occurs, it appears that the observed relationship, while it may be empirical, can nevertheless be useful in predicting formation constants of weak complexes from line width experiments. Several other alkali metal complexes are being investigated in the hope of extending the usefulness of this relationship.

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(3) G. A. Rechnitz and S. B. Zamochnik, *ibid.*, in press.

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RECEIVED MARCH 14, 1964

Mercury-Photosensitized Reactions between Paraffins and Tritium. A Simple, Rapid, and Selective Tritiation Technique

Sir:

Alkyl radicals, hydrogen atoms, and tritium atoms are formed in the mercury-sensitized photolysis of paraffin-T₂ systems. The alkyl radicals have the same carbon number as the parent paraffin, because no C-C bond rupture occurs.¹ Thus at high intensities where radical recombinations ($R + T \rightarrow RT^*$) are favored, a single tritiated product, namely, the tritiated parent compound, should predominate provided the paraffin gas pressure is sufficiently high so that the excited species formed in the recombination rapidly undergoes collisional deactivation. This suggests a simple procedure which may add both speed and selectivity to the versatile Wilzbach² tritiation method.

In the Wilzbach method, the compound to be tritiated is simply mixed with T₂, which initiates the reaction by undergoing β -decay. The speed of this tritiation reaction can be increased by subjecting the mixture to electrical discharge,³⁻⁶ microwave,^{5,6} and γ -rays,^{7,8} but these methods increase C-C bond rupture, and no significant improvement in the selectivity has been reported.

The mercury-sensitized reaction between ethylene and tritium⁹ gives various tritiated products expected from reactions between T atoms and ethylene. In the olefin reactions, selectivity is neither expected nor found. Liquid cyclohexane (together with other compounds) has also been tritiated, but the selectivity was not reported.¹⁰ Probably, the major tritiation reactions proceeded in the vapor phase where excessive cracking of the excited species would be expected to occur because of low vapor pressure.

In the present experiments, 600 mm. of a paraffin gas together with 2.2 c. of T₂ (4.68 mm. at 150 cc.) were introduced in a 150-cc. Vycor cell (which contained a drop of mercury at room temperature). After 1 min. of ultraviolet irradiation with a low-pressure mercury lamp (Hanovia 94A-1, 575 v. and 0.120 amp.), tritiated products were analyzed by using a temperature-programmed gas chromatograph in which a 10-cc. ionization chamber was incorporated.¹¹ Comparison of the distribution of tritiated products in photolysis and in self-radiolysis provides important information on radiolysis mechanisms. For this reason, the products of self-radiolysis were also analyzed. The methane mixture was allowed to stand for 2.4 hr., while the other mixtures were radiolyzed for 100 hr.

Table I gives the rate of formation of tritiated parent

(1) For recent investigations, see (a) R. A. Back, *Can. J. Chem.*, **37**, 1834 (1959); (b) R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **67**, 2273 (1963).

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(8) K. Yang and P. L. Gant, *J. Chem. Phys.*, **31**, 1589 (1959).

(9) I. Kaplan, *J. Am. Chem. Soc.*, **76**, 1448 (1954).

(10) F. Cacace, A. Guarino, and G. Montafinale, *Nature*, **189**, 54 (1961).

(11) Paraffins and tritium were thoroughly purified: see K. Yang and P. L. Gant, *J. Phys. Chem.*, **65**, 1861 (1961); **66**, 1619 (1962). Hydrocarbon impurities in methane were removed by low-temperature chromatography.

TABLE I

THE RATE OF FORMATION OF TRITIATED PARENT COMPOUNDS IN THE PHOTOLYSIS AND RADIOLYSIS OF PARAFFIN-T₂ (2.2 c.) SYSTEMS

		Methane	Ethane	Propane	n-Butane	Isobutane	Neopentane
Ultraviolet rate	{ mc./min.	57.4	65.6	3.34	0.845	0.695	70.0
	{ molecules/photon	0.22	0.25	0.013	0.0033	0.0027	0.27
β-Rate	{ (mc./min.) × 10 ⁴	14.3	0.678	0.462	0.305	0.337	0.359
	{ (molecules/100 e.v.) × 10 ²	10.9	0.52	0.35	0.23	0.26	0.27

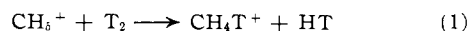
TABLE II

DISTRIBUTION OF TRITIATED PRODUCTS^a

	Irradiation	Methane	Ethane	Propane	n-Butane	Isobutane	Neopentane	Dimer
Methane	Ultraviolet	100	0.10	0.03	0.01	0.03	...	0.1
	β	100	131	33	7	6
Ethane	Ultraviolet	8	100	5	9	0.2	...	9
	β	38	100	140	51
Propane	Ultraviolet	0.2	0.2	100	3	2	...	21
	β	76	20	100	23	21
n-Butane	Ultraviolet	100	()
	β	62	36	14.0	100	()
Isobutane	Ultraviolet	100	...	12.3
	β	140	0.7	14	...	100
Neopentane	Ultraviolet	0.4	0.1	0.1	...	0.6	100	()
	β	133	24	17	...	32	100	()

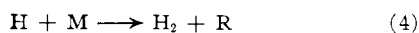
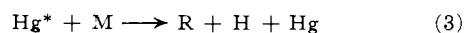
^a ... signifies <0.01, while () denotes not analyzed.

compounds in photolysis and self-radiolysis. In comparison with other self-radiolysis rates, the methane self-radiolysis rate is very much higher. This is attributable to the high yield ($G = 1.9$) of CH_5^+ ions¹² which supposedly undergo the reactions¹³

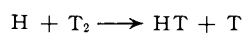


Apparently, the corresponding reactions are unimportant in other radiolyses. The ultraviolet irradiation accelerates the tritiation 4×10^4 to 2×10^6 times, depending on the paraffins employed. The photon-input rate determined by using an ethylene dosimeter,¹⁴ in which $\phi_{(\text{H}_2)}$ in the mercury-sensitized photolysis of ethylene at 13 mm. was taken to be 0.570, was 8.7×10^{-6} mole of photons/min.; hence the number of T atoms incorporated in propane per photon absorbed by mercury atoms becomes 0.013. Because of the lack of information on T_2 -quenching cross section, a further quantitative discussion of the tritiation yield is not justified at present.

The tritiation rate in photolysis is expected to slow down as the rates of the reactions



increase, because then two competing reactions



producing T atoms become slower. Both eq. 3 and 4 are more important when C-H bond strengths are lower. On this basis, the trend evident in Table I is explainable with the exception of methane. In the methane reaction, [T] is probably high, and some three-body recombination producing T_2 can occur.

Table II summarizes the distribution of tritiated products. Both in radiolysis and photolysis, an arbitrary

value of 100 is assigned to the tritiated parent product. In the photolysis of methane, tritiated methane is the only important product. The negligible ethane yield indicates that tritiated methyl radicals are not formed. Gas chromatographic analysis showed that only monotritiated methane is formed.¹⁵ These observations are in agreement with the results in methane-deuterium systems, for which a detailed mechanism study has already been published.¹⁶ Negligible yields of high molecular weight products indicate that chain lengthening by a radical process is not occurring. This disagrees with the conclusion obtained by using NO in methane radiolysis.¹⁷ Evidently, NO reacts with high molecular weight ions.¹² In sharp contrast to the photolysis, methane radiolysis produces large amounts of high molecular weight tritiated products. Tritiated ethane but not methane is most abundant. This observation is consistent with the high G -value of 0.9 for C_2H_5^+ ions in radiolysis.¹² Tritiated propane and butanes are also formed in significant amounts; and it seems necessary to invoke chain lengthening by ionic mechanisms, as observed in mass spectrometric experiments at high pressures,¹⁸ to provide explanation.

Ethane is the only compound showing appreciable C-C bond rupture in the photolysis. Tritiated methyl as well as ethyl radicals seem to be formed. The latter probably come from the reaction of T atoms with ethylene produced in the disproportionation reaction between two ethyl radicals. The selectivity, however, is still greatly improved over radiolysis, where excessive C-C bond rupture as well as chain lengthening occurs. In view of the high yield of tritiated propane, reactions corresponding to those producing C_2H_5^+ ions in methane radiolysis may be important in ethane radiolysis.

In the photolysis of C_3 to C_5 paraffins, practically no C-C bond rupture occurs. The only significant products other than tritiated parent compound are tri-

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(14) K. Yang, to be published.

(15) K. Yang and P. L. Gant, *J. Am. Chem. Soc.*, in press.(16) R. F. Firestone, C. F. Lemr, and G. J. Trudel, *ibid.*, **84**, 2279 (1962).(17) K. Yang and P. J. Manno, *ibid.*, **81**, 3507 (1959).(18) S. Wexler, *ibid.*, **85**, 272 (1963).

tiated dimers, which are likely formed by the internal scavenging reactions mentioned above. Usually, however, boiling points of parent and dimer products are so far apart that the removal of the latter poses no problem. When this step is taken, mercury-sensitized photolysis in paraffin-tritium systems provides a simple, rapid, and highly selective method for tritiating gaseous paraffins.

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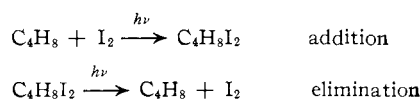
RECEIVED MARCH 21, 1964

Stereospecific *trans* Photoaddition of Elementary Iodine to Aliphatic Olefins. Bridged Iodoalkyl Radicals

Sir:

The literature contains few references to the synthesis of aliphatic vicinal diiodides and it is the general impression that these substances are both difficult to synthesize and are unstable, decomposing to elementary iodine and the corresponding olefin.¹ We can report that elementary iodine adds readily under illumination to 1-butene,² the 2-butenes, and isobutene at -40° to produce colorless crystalline diiodides. Decomposition of these diiodides to starting materials occurs at room temperature.

Additions are conveniently carried out in refluxing propane (-42°) with illumination from a tungsten filament lamp. With reactive olefins, decolorization of a mixture of 1 g. of iodine and 10 g. of olefin in 50 ml. of propane usually occurs within 30 min. under illumination, although occasionally the reaction is slower, suggesting that oxygen or perhaps other substances can inhibit the additions. A comparable dark reaction for several hours does not result in extensive loss of iodine. The colorless diiodides are isolated in quantitative yield by pumping off solvent and unreacted olefin. Samples have been kept in the dark at -78° for days without decomposition. At room temperature the iodides decompose rapidly to the original reactants in a reaction which is accelerated by illumination. The olefin can be isolated by pumping under high vacuum through a -78° trap which stops the iodine but allows the olefin to pass through. In each case pure olefin was recovered in yields greater than 90%, and in one case the trapped iodine was weighed and found to be 88.5% of the original.

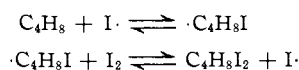


The addition-elimination cycle applied to *cis*- and *trans*-2-butenes yielded colorless diastereomeric 2,3-diiodobutanes, m.p. -24 to -23° , and -11° dec. Decomposition at room temperature converted the diiodides to the respective starting olefins in better than 90% yields and purities identical with the original. Thus, both addition and elimination reactions are stereospecific.

(1) T. S. Paterson and J. Robertson, *J. Chem. Soc.*, **125**, 526 (1924); A. Fairbourne and D. W. Stevens, *ibid.*, 1973 (1932); M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957); F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958); S. J. Cristol, L. K. Gaston, and T. Tiedeman, *J. Am. Chem. Soc.*, in press.

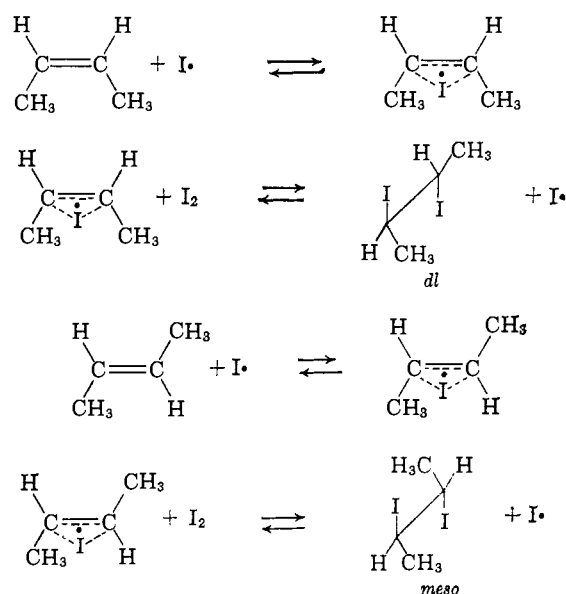
Two lines of evidence indicate these stereospecific addition reactions occur with a *trans* geometric requirement. (a) Dehalogenation of the diiodides with zinc dust in methanol at -78° regenerates the olefin from which it had been prepared. A similar procedure, applied to the known 2,3-dibromobutanes, generates olefins by a stereoselective *trans* elimination.³ (b) The *dl*- and *meso*-2,3-dichloro- and -dibromobutane isomer pairs show similar characteristic differences in δ for the proton magnetic resonance absorptions of the CH_3 and the CH groups. The same differences occur in the spectra of the diastereomeric diiodides. If the analogy is applicable, the *meso*- and *dl*- forms are identified. Methods (a) and (b) are in agreement, thus identifying the diiodides, *meso*, m.p. -11° dec., and *dl*, m.p. -24 to -23° .

The slow dark reaction, photoacceleration of *trans* additions, erratic rates of reaction, and *trans* photodecompositions are best explained by the hypothesis of a radical chain mechanism.



Evidence has been presented³⁻⁵ which requires a bridged radical structure for β -bromo and β -chloroalkyl radicals. Unpublished work has established the order of bridge stabilities, $\text{F} \ll \text{Cl} < \text{Br}$, and this suggests that the most effective bridging halogen in β -haloalkyl radicals should be iodine, just as for β -bridging in carbonium ions.

The observations reported here are best rationalized by assigning bridge structures to the radical intermediates.



Acknowledgment.—Financial assistance from the Air Force Office of Scientific Research and Development is gratefully acknowledged.

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- (4) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).
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RECEIVED MARCH 23, 1964