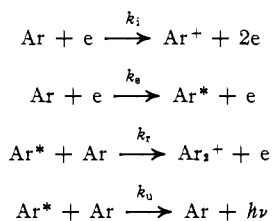


effective lifetime of 1.1×10^{-6} sec., are involved in Ar_2^+ formation. Combination of this value with the results of Dahler, *et al.*,³ yields a rate constant for Ar_2^+ formation of 3.2×10^{-10} cm.³ molecule⁻¹ sec.⁻¹.

The pulse method of determining thermal rate constants of ion-molecule reactions, described by Tal'roze and Frankevich,⁵ seems to afford an opportunity to obtain k and τ separately and has been applied in this laboratory to the second-order formation of Ar_2^+ . In this method a pulsed electron beam is followed after a variable delay time by a pulsed ion-extraction field. Thus, with a large extraction field, the reaction time may be taken as the delay time plus any reaction time during the finite electron pulse.

For application to the second-order Ar_2^+ formation, consider the mechanism of Dahler, *et al.*,³ *viz.*



From this mechanism and the relationship

$$[\text{Ar}^*]_{t=0} = \left(\frac{k_e}{k_i}\right)[\text{Ar}^+]$$

it is easily shown that

$$\frac{[\text{Ar}_2^+]}{[\text{Ar}^+]} = \frac{\left(\frac{k_e}{k_i}\right)k_r[\text{Ar}]}{k_u + k_r[\text{Ar}]} \left\{ 1 - e^{-(k_u + k_r[\text{Ar}])(t_d + t_0)} \right\} \quad (1)$$

where t_d is the delay time and t_0 is the reaction time during the electron pulse.

Measurements of $[\text{Ar}_2^+]/[\text{Ar}^+]$ (assuming it may be equated to the ion-current ratio I_{80}/I_{40}) have been carried out as a function of delay time, t_d , in a Bendix 14-101 time-of-flight mass spectrometer which has been modified by incorporating a closed ion source and differential pumping. The ion source was calibrated for gas concentration using the known rate of formation of CH_5^+ in methane.⁵ Mass-dependent diminution of the ion beam occurs with increasing delay time so that it was necessary to construct discrimination curves at the pertinent masses and to correct all ion currents for this intensity decrease. In all experiments the nominal electron beam energy was that of the maximum in the Ar_2^+ ionization efficiency curve. At this electron energy, Dahler, *et al.*,³ found $(k_e/k_i) = 0.055$.

The results for three pressures of argon are shown in Fig. 1. Here it can be seen that the general shape predicted by eq. 1 is obtained and that, moreover, the curves extrapolate to the time axis at a time that corresponds to $t_0 = 0.12 \pm 0.02$ μsec . This is quite consistent with our measured pulse width and rise time of 0.25 and 0.11 μsec ., respectively.

From best fits of the data, according to eq. 1, for the two higher pressures and the value³ of 0.055 for k_e/k_i we find $k_r = 4.3 \pm 0.3 \times 10^{-10}$ cm.³ molecule⁻¹ sec.⁻¹ and $k_u = 1/\tau_u = 2.1 \pm 0.2 \times 10^6$ sec.⁻¹. The lowest pres-

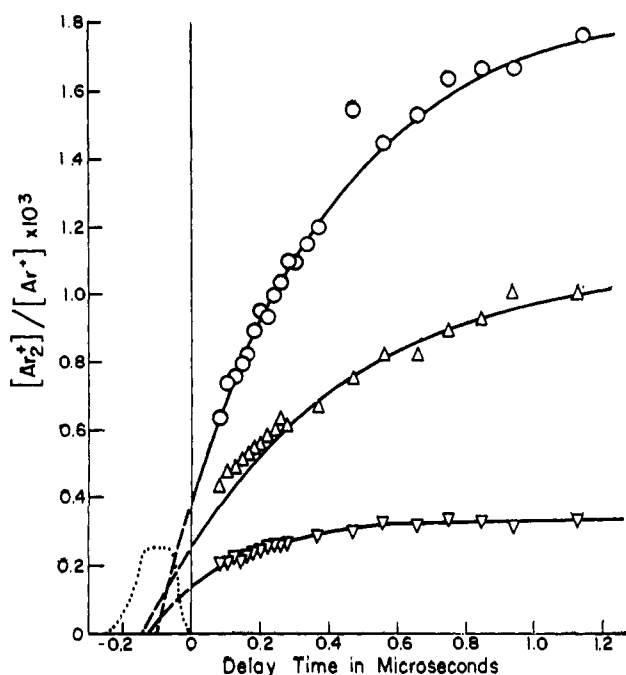


Fig. 1.—Dependence of ion-current ratio on delay time. Ar source pressures (microns): O, 5.2; Δ , 3.0; ∇ , 1.0;, electron beam pulse.

sure was not used in the determination of rate constants since reaction is nearly over even at the shortest delay times used.

The value of $k_r\tau_u$ from our work is 2.1×10^{-16} cm.³ molecule⁻¹ which is to be compared with 3.6×10^{-16} found by Dahler, *et al.*³ Considering uncertainties in the source concentrations and the diversity of the experiments, the agreement is satisfactory. Our value for τ_u of 4.8×10^{-7} sec. is in satisfactory agreement with the work of Kaul.⁴ The value found for k_r corresponds to a cross section of the same order of magnitude as those of ordinary gas collisions.

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Correlation of Nuclear Spin Resonance Line Widths with Formation Constants of Weak Complexes

Sir:

In 1960, Jardetzky and Wertz¹ reported an observed broadening of the nuclear spin resonance absorption line of Na^{23} in the presence of certain anions and attributed this effect to an interaction of the Na^{23} nuclear quadrupole with an electric-field gradient caused by the formation of weak complexes of sodium with the added anions. Unfortunately, owing to the lack of independent data concerning such weak complexes, this interesting hypothesis could not be experimentally confirmed or examined for quantitative utility at that time.

(5) V. L. Tal'roze and E. L. Frankevich, *Zh. Fiz. Khim.*, **34**, 2709 (1960).

(1) O. Jardetzky and J. E. Wertz, *J. Am. Chem. Soc.*, **82**, 318 (1960).

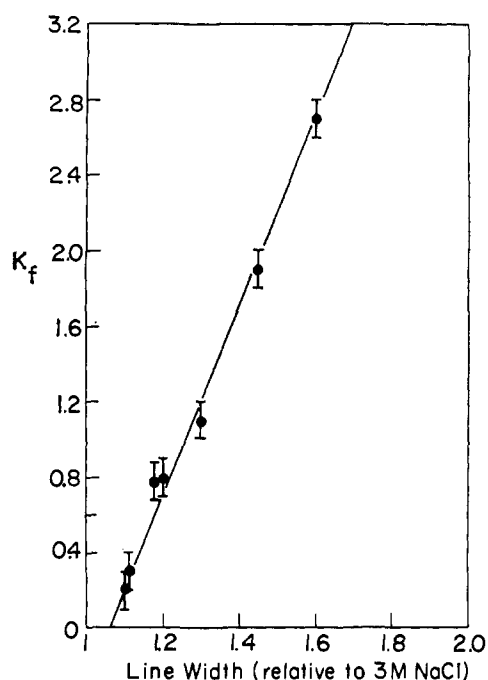


Fig. 1.—Plot of line width vs. formation constant for sodium complexes.

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.

(2) G. A. Rechnitz and J. Brauner, *Talanta*, **11**, 617 (1964).

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

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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

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(7) R. W. Ahrens, M. C. Sauer, and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 3284 (1957).

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

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(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.