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receives support from the appearance of definite threshold angles in several other systems K+CH₃Br,¹⁴ $K+CH_3I$ ¹⁵ K+HCl³ $Na+CH_3I$ ¹¹ $Na+C_2H_4Br_2$ ¹¹ and K+SF₆.¹⁵ For further discussion of our simple

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model, see Ref. 15. These kinematic upper limits for r_m force the selection of values below the lower end of the range given in Sec. IV. Thus our recommended values for r_m are: K+HBr, 4.2 Å; K+DBr, 3.9 Å. For this work we have arbitrarily chosen to use the exp-6 potential with $\alpha = 12$. A reduction in α or another model for the potential might bring the two estimates of r_m into better agreement.

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Scattering of Potassium by a Series of Reactive and Nonreactive Compounds in Crossed Molecular Beams*

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(Received 23 November 1966)

The scattering of potassium by the nonreactive compounds C(CH₃)₄, C₆H₆, C₆H₁₂, (CH₃)₂C=C(CH₃)₂ and the reactive compounds CH₃I, CCl₄, SiCl₄, SnCl₄, SF₆ has been studied in experiments with crossed molecular beams. In each case the nonreactive scattering of velocity-selected K was measured as a function of laboratory scattering angle at a number of initial relative kinetic energies. Except for K+SnCl₄, rainbow scattering is observed. The differences which appear between the measured scattering in this region for the various nonreactive compounds show the influence of the molecular structure on the intermolecular potential. Potential parameters of an assumed spherically symmetric potential (exp-6, $\alpha = 12$) are calculated from the rainbow scattering. The scattering of K from the various reactive compounds differs markedly at larger angles and is an indication of a correspondingly large variation of reaction cross sections. Probabilities of reaction, threshold energies, threshold distances, and the energy dependence of the total reaction cross sections are obtained from an interpretation of the measurements.

I. INTRODUCTION

MOLECULAR-beam techniques have revealed some interesting details of the dynamics of elementary chemical reactions. In this article we report on measurements of potassium scattered from two series of compounds. The first is a group of nonreactive compounds chosen to show some of the effects of molecular structure on the differential scattering cross section. The second is a group of compounds which show the additional effects of varying chemical reactivity.

Information about reactions is obtained both from measurements on the scattered reactants, as in the present work, and from measurements on the products. Fortunately, for several systems a comparison is possible of the interpretations of both kinds of measurements because a number of the compounds reported on here, as well as similar substances, have been studied by several groups.¹⁻⁵ These comparisons show encouraging agreement.

II. EXPERIMENTAL

The apparatus has been described.⁶⁻⁸ All the experiments were made with the out-of-plane arrangement of the detector and the molecular beams in which the cross beam, perpendicular to the K beam, is also perpendicular to the plane of motion of the detector (see Fig. 1, Ref. 8). As in Ref. 8, a Pt surface ionization detector with two Pt ribbons was used to provide different angular resolutions. The K beam emerged

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						Operati	ng speed	Referenc	e speed°
System	Run	(kcal/ mole)	^v 10 (m/sec)	Detector	$M^{ m b} \!$	% atten- uation	$e^{\Omega N_K^0 \times} imes 10^{12} \mathrm{A}$	% atten- uation	$e^{\alpha N_{K}^{0}}$ $ imes 10^{12}$ A
K+C(CH ₃)4	1 2 3 4 5 6	1.30 1.30 1.30 2.18 3.71 5.36	586 586 586 795 1067* 1297	N W N N N N	3.0 3.1 3.0 2.6	16 17 7 16 8 11	60.5 58.0 61.4 438 720 435	$ 11 \\ 11 \\ 11 \\ 14 \\ 8 \\ 12 $	70.5 70.5 70.5 677 720 720
$K + C_6 H_6$	7 8 9	2.22 3.65 5.48	796 1046* 1297	N N N	27.0 27.0 20.0	15 13 11	439 740 451	13 13 13	740 740 740
K+C ₆ H ₁₂	10 11 12	$2.25 \\ 4.31 \\ 5.60$	795 1129* 1297	N N N	9.0 8.8 11.0	11 8 8	1990 1275 1990	9 8 8	985 1275 1192
$K+(CH_3)_2C=(CH_3)_2$	13 14 15 16	$ 1.85 \\ 1.85 \\ 3.45 \\ 5.60 $	711 711 1004* 1297	N N N N	15.0 15.0 18.0 16.0	12 16 9 9	254 186 1250 600	9 12 9 9	1278 820 1250 1278
K+CH ₈ I	17 18 19 20 21 22	1.42 1.42 2.99 4.17 5.55 6.72	586 586 878* 1046 1213 1338	N W N N N N	7.0 ^d 7.8 8.1 11.0 12.0	15 15 14 11 11 10	70 69 1500 2125 1240 752	14 14 14 14 14 14	1500 1500 1500 1500 1500 1500
K+CCl4	23 24 25 26	2.04 3.31 4.90 6.83	711 920 1129* 1338	Ň N N	5.7 5.2 4.7 5.4	15 12 12 10	395 1460 1147 575	10 11 12 11	1190 1345 1147 1288
K+SiCl4	27 28 29 30	2.06 3.36 5.35 6.94	711 920* 1171 1338	N N N N	10.0^{d} 11.0 7.9 9.3	11 10 9 6	331 2260 380 1500	9 10 11 8	2110 2260 507 2110
K+SnCl ₄	31 32 33 34 35	2.15 3.86 5.67 7.38 7.38	711 962* 1171 1338 1338	N N N N		12 14 9 9	244 666 738 398 327	9 14 10 11 14	730 666 770 796 666
K+SF6	36 37 38 39 40	1.42 2.02 3.57 5.21 6.76	586 711 962* 1171 1338	N N N N	3.0 3.4 4.3 5.7 38.0	14 20 11 20 9	77 207 704 1180 912	10 18 11 21 11	321 1220 704 1150 1680

TABLE I. Experimental conditions for the measurements.ª

^a The symbols are defined in the text, Sec. II.

^b Measurements made with wide detector (W) are normalized to comparable runs made with narrow detector (N).

° Reference speeds are marked by asterisks in column v_{10} .

d Guessed value.

from a single exit channel which was a hypodermic needle.⁸

The chemicals were of reagent grade and were not purified further. Gas-chromatographic analyses were made on all the chemicals (except CH_3I and $SnCl_4$) and showed impurities of less than 1%.

The experimental conditions are given in Table I, where the symbols denote the following:

$$\bar{E} = \frac{1}{2} \mu (v_{10}^2 + \bar{v}_2^2),$$

the initial relative kinetic energy; μ , the reduced mass of the reactants; v_{10} , the central K speed transmitted by the velocity selector; $\bar{v}_2 = (8kT_2/\pi m_2)^{1/2}$, the average speed of the cross-beam molecules of mass m_2 at the source temperature T_2 (295°K for all measurements); M, a constant (see below); $N_{\rm K}$ °, the flux (molecules per square centimeter second) arriving at the detector, located at the laboratory angle $\alpha = 0$, in the absence of the cross beam; α , the cross-sectional area of the K beam; and e, the elementary charge.

III. MEASUREMENTS

The experimental results for the nonreactive scattering of K by C(CH₃)₄, C₆H₆, C₆H₁₂, (CH₃)₂C=C(CH₃)₂, CH₃I, CCl₄, SiCl₄, SnCl₄, and SF₆ are shown in Figs. 1-9, respectively. The ordinates are proportional to a differential scattering cross section as measured by a detector of finite size and are labeled $M \langle \sigma_{\text{eff}}(\alpha) \rangle_D \sin\alpha$. See Eq. (1) of Ref. 8. The symbol D indicates an average over the area of the detector, the subscript "eff" indicates an effective cross section measured at an average initial kinetic energy \tilde{E} , and $\alpha,\beta=\frac{3}{2}\pi$ are lab-



FIG. 1. K+C(CH₃)₄, differential laboratory cross section for nonreactive scattering, multiplied by $M \sin \alpha$, $M \langle \sigma_{eff}(\alpha) \rangle_D \sin \alpha$, for four relative energies, vs laboratory angle in degrees.

oratory scattering angles (see Eq. 1, Ref. 8, ff). For the given reference speed, M is a proportionality constant which is determined for each run by matching the experimental results to the quantity $Mr_m^2[\sigma_c(\alpha)/r_m^2] \sin \alpha$, where r_m is a size parameter of the potential of interaction and $\sigma_c(\alpha)/r_m^2$ is a calculated, reduced cross section for elastic scattering. The angle α chosen for this matching varies from system to system, but is in an angular region in which we assume the scattering is unaffected by reaction.



FIG. 2. $K+C_6H_6$, differential laboratory cross section for nonreactive scattering, multiplied by $M \sin \alpha$, $M \langle \sigma_{eff}(\alpha) \rangle_D \sin \alpha$, for three relative energies, vs laboratory angle in degrees.



FIG. 3. K+C₆H₁₂ (cyclohexane), differential laboratory cross section for nonreactive scattering, multiplied by $M \sin \alpha$, $M \langle \sigma_{\rm eff}(\alpha) \rangle_D \sin \alpha$, for three relative energies, vs laboratory angle in degrees.



FIG. 4. $K + (CH_3)_2 C=C(CH_3)_2$, differential laboratory cross section for nonreactive scattering, multiplied by $M \sin \alpha$, $M \langle \sigma_{eff}(\alpha) \rangle_D \sin \alpha$, for three relative energies, vs laboratory angle in degrees.

IV. POTENTIAL PARAMETERS

Rainbow scattering is observed in the nonreactive scattering of K by all compounds studied here except $SnCl_4$. Supernumerary rainbows are just visible in some cases, e.g., Runs 24 and 25; the resolution is not sufficient for the detection of the fine structure due to quantum mechanical interferences from all three branches of the deflection function.²

Potential parameters have been determined from the rainbow scattering (Tables II, III) by assuming that the scattering of K is semiclassical elastic scattering and by assuming that this elastic scattering is described by the centrosymmetric exp-6 potential [Eq. (1)] Ref. 7]. The details of calculating potential parameters are given by Method A of Sec. IV, Ref. 8. Possible sources of error in this determination are: (1) reactive and inelastic collisions may affect the observed scattering in the rainbow region; (2) the interaction potential may depend on orientation as well as distance, particularly for systems like $K+CH_3I$, $K+C_6H_6$; (3) the spherically symmetric part of the potential may not be well represented by an exp-6 potential; (4) the semiclassical theory may be inadequate, particularly at low energies; (5) remaining distributions of relative kinetic energy and beam intersection angles may affect the observed scattering.

We now comment on some of these points. Reactive collisions affect the observed scattering of K for all the reactive systems studied here. The rainbow scatter-

ing in the systems $K+CH_3I$, SiCl₄, and SF₆ does not seem to be influenced by the possibility of reaction, although we note, without understanding why, that the r_m are unexpectedly low and rainbow maxima are less pronounced in $K+SiCl_4$ than in the other systems. For $K+SnCl_4$, reaction apparently occurs with high probability at such large impact parameters that no rainbow scattering is observed. For $K+CCl_4$, the reaction seems to occur at impact parameters corresponding to elastic scattering angles close to the rainbow region. We have no information on the effect of inelastic collisions.

In Table II we list available values of the anisotropy of the polarizability, a quantity of direct influence on the anisotropy of the interaction potential. A comparison of the scattering of K with benzene and cyclohexane shows that the rainbow scattering region extends over a much larger range of scattering angles in C_6H_6 than



FIG. 5. K+CH₃I, differential laboratory cross section for nonreactive scattering, multiplied by $M \sin \alpha$, $M \langle \sigma_{\rm eff}(\alpha) \rangle_D \sin \alpha$, for five relative energies, vs laboratory angle in degrees.

 C_6H_{12} . Qualitatively this may be related to the much larger anisotropy of the polarizability of C₆H₆. A larger anisotropy implies a larger range of the potential parameter ϵ as the orientation of C₆H₆ varies relative to K. In this view, the observed scattering of K from C₆H₆ is an average of the scattering from various orientations, and this average results in a widening of the angular range of the rainbow scattering corresponding to the range of ϵ . As a further consequence of this averaging the slope of the rainbow pattern, from the maximum to larger angles, is expected to be smaller than that for the scattering from a spherically symmetric potential. Hence, our determination yields size parameters for $K+C_6H_6$ which are substantially too small. We also note that the angular extent of the observed rainbow scattering for $K+C_2(CH_3)_4$ is about in between that of $K+C_6H_6$ and $K+C_6H_{12}$.

Errors introduced by the use of a semiclassical theory and by the neglect of the remaining energy distribution affect the determination of the size parameter r_m much



FIG. 6. K+CCl₄, differential laboratory cross section for nonreactive scattering, multiplied by $M \sin \alpha$, $M \langle \sigma_{eff}(\alpha) \rangle_D \sin \alpha$, for four energies, vs laboratory angle in degrees.



FIG. 7. K+SiCl₄, differential laboratory cross section for nonreactive scattering, multiplied by $M \sin \alpha$, $M \langle \sigma_{off}(\alpha) \rangle_D \sin \alpha$, for four relative energies, vs laboratory angle in degrees.

more than that of the energy parameter ϵ . We estimate that these errors may amount to 3% in ϵ but about 10% in r_m .⁹

The energy parameter ϵ is apparently constant over our range of energy \tilde{E} , within the experimental uncertainty for the nonreactive systems, but the size parameter for these systems shows a possibly significant increase with increasing energy. For the reactive systems both ϵ and r_m increase with energy, usually r_m more than ϵ .

Without any explanations for the trends in the potential parameters with energy, we simply average the values of the parameters of each system and take the maximum deviation from these averages as an estimate of the error (Tables II, III).

V. INTERPRETATION OF RESULTS FOR REACTIVE SYSTEMS

The scattering of K at large angles from nonreactive systems differs from that for reactive systems. Previously we have ascribed such differences to reaction

 $^{^{9}}$ E. F. Greene, G. P. Reck, and J. L. J. Rosenfeld (private communication).



FIG. 8. K+SnCl₄, differential scattering cross section for nonreactive scattering, multiplied by $M \sin \alpha$, $M \langle \sigma_{\text{eff}}(\alpha) \rangle_D \sin \alpha$, for four relative energies, vs laboratory angle in degrees.

and have given a simple classical interpretation.^{6,7} We continue with this approach for the reactive systems and also make a comparison of the measurements with optical model calculations and previous work.

A. Probability of Reaction and Threshold Values

The differential cross section for the scattering of K from CH₃I, and SF_v, Figs. 5 and 9, shows, at each energy but the lowest, a decrease in slope at scattering angles larger than the rainbow region. This may be contrasted with the behavior of the nonreactive analogs, e.g., C(CH₃)₄. According to the interpretation presented previously, this decrease in slope occurs at an angle, the threshold angle, at which the reduced impact parameter β , or the reduced distance of closest approach y, is sufficiently small for reaction to occur. Furthermore, if the reactants are considered to interact as two particles, then the potential of that interaction at the threshold distance is V(y), which is taken to be an exp-6 potential ($\alpha = 12$) with the potential parameters determined from the rainbow region. Hence χ the relative scattering angle, β and V(y) are related through the classical equations of motion. The probability of reaction is assumed to be

$$P[\bar{E}, V(y)] = [\sigma_c(\bar{E}, \chi) - \sigma(\bar{E}, \chi)] / \sigma_c(\bar{E}, \chi), \quad (1)$$

where $\sigma_c(\bar{E}, \chi)$ is the classical differential scattering cross section calculated with the determined potential parameters. This probability of reaction is shown in Fig. 10, and the threshold conditions are listed in Table III.

The scattering of K from the reactive molecule CCl_4 is also markedly different at large scattering angles from that of $C(CH_8)_4$. However, no changes in slope are observed to mark the threshold angles; this is similar to the scattering of K by HBr and DBr.⁸ We follow therefore the procedure outlined in Ref. 8 and



FIG. 9. K+SF₆, differential laboratory cross section for nonreactive scattering, multiplied by $M \sin \alpha$, $M \langle \sigma_{eff}(\alpha) \rangle_D \sin \alpha$, for five relative energies, vs laboratory angle in degrees.

Compound	Molecular polarizability,* cm ³ ×10 ²⁵	Anisotropy in polarizability, ^a $(\alpha_1 - \alpha_2) / (\alpha_1 + 2\alpha_2)$	Run	$ar{E}$ (kcal/mole)	(kcal/mole)	$r_{m,b}$ (Å)
C (CH ₃) ₄	110°	0	2 4 5 6	1.30 2.18 3.71 5.36 (Average)	$\begin{array}{c} 0.520 \\ 0.506 \\ 0.530 \\ 0.566 \\ 0.53 \pm 0.03 \end{array}$	$3.713.267.056.505.1\pm1.9$
C_6H_6	103	0.284	7 8 9	2.22 3.65 5.48	0.577 0.605 0.608	1.49 1.96 2.69
				(Average)	0.59 ± 0.02	2.0 ± 0.7
$C_{6}H_{12}$	109	0.075	10 11 12	2.25 4.31 5.60	0.666 0.644 0.686	2.38 3.58 3.84
				(Average)	$0.66 {\pm} 0.03$	3.3 ± 0.9
C ₂ (CH ₃) ₄	120°		14 15 16	1.85 3.45 5.60 (Average)	0.562 0.594 0.535 0.56±0.03	2.32 2.89 3.47 2.9±0.7

TABLE II. Nonreactive systems. Parameters for exp-6 ($\alpha = 12$) potential.

^a Landolt-Börnstein Zahlenwerte und Functionen, A. M. Hellwege and K. H. Hellwege, Eds. (Springer-Verlag, Berlin), Vol. 1, Pt. 3 (1951), p. 510 ff; Vol. 2, Pt. 6 (1959), p. 872 ff.

^b r_m values are probably low particularly in the case of C₆H₆, see text. ^c Estimated from bond polarizabilities.

use Eq. (9) of that paper for the calculation of $\sigma_c(\bar{E}, \chi)$, except that we use simply the unaveraged Airy function, Ai^2 , and omit the estimated correction for the semiclassical theory. The probability of reaction is also shown in Fig. 10, and the threshold conditions are listed in Table III. The calculated threshold angles are close to the rainbow region and it is possible that the structure in the rainbow region is affected by the reaction due to the diminution of elastic scattering from the innermost branch of the classical deflection function. Such a distortion of the rainbow scattering would lead to energy parameters ϵ decreasing with decreasing relative kinetic energy. However, we do not know to what extent the observed trend of ϵ with \bar{E} may be due to this effect.

The scattering of K from SnCl₄ shows no rainbow structure. There is, however, some structure in the graphs in Fig. 8 which becomes more visible in a plot of the logarithm of the nonreactive differential scatter-





ing cross section in relative coordinates [obtained from $\langle \sigma_{\rm eff}(\alpha,\beta) \rangle_D \sin \alpha$ by use of Eqs. (6) and (7) of Ref. 8] vs the logarithm of the relative scattering angle. Such curves are shown in Fig. 11. The points plotted there are *not* corrected for the size of the detector. The

FIG. 11. K+SnCl₄, logarithm of the differential scattering cross section in relative coordinates multiplied by $M \sin \chi$, $[M \langle \sigma_{\text{eff}}(\chi) \rangle_D \sin \chi]$, for four relative energies, vs the logarithm of the relative scattering angle χ in degrees. Dashed lines: prediction for scattering according to a potential $V(r) \sim r^{-6}$. Solid lines: drawn to fit the points at larger angles.



$\Delta E_0^{\circ \bullet}$ po (kcal/ 1 Compound mole) (X					From rainbow scattering		At threshold									
	Molecular polariza- bility ^b (×10 ²⁵ cm ³)	Anisotropy of polariza- bility ^b	Run	$ar{E}_{(ext{kcal}/mole)}$	€ (kcal/ mole)	ř _m (Å)	α (deg)	x (deg)	у	V(y) (kcal/ mole)	β	$\sigma_{R^{0}}/\tau_{m^{2}}$ L	r _m ^d (Å)	$({}^{\sigma_R}{}^{d}, ({}^{A^2})$		
CH ₁ I	-22	80	0.098°	18	1.42	0.452		53.6	62.0	0.855	0.35	0.750	1.11			
				19	2.99	0.498		27.0	33.2	0.867	0.11	0.848	1.64			
				20	4.17	0.526		22.5	28.0	0.862	0.19	0.841	1.75	210	4.8	50
				21	5.55	0.549		17.1	21.4	0.867	0.11	0.859	1.94			
				22	6.72	0.529		14.3	18.0	0.873	0.04	0.872	2.03			
					(Average)	$0.51 {\pm} 0.06$										
CCI4	-31	105	0	23	2.04	0.655	3.71	36.6	43.5	0.869	0.10	0.844	2.12			
				24	3.31	0.672	5.72	23.5	28.6	0.875	0.01	0.872	2.11			
				25	4.90	0.700	6.09	16.2	20.0	0.883	-0.10	0.893	2.30	250	4.6	50
			26	6.83	0.748	6.41	12.5	15.5	0.886	-0.15	0.899	2.42				
			(Average)	0.69±0.06	5.5 ± 1.8											
SiCl4	-14	134	0	27	2.06	0.625	1.44									
				28	3.36	0.642	3.09							63		6
				29	5.35	0.661	3.04									
				30	6.94	0.674	3.83									
					(Average)	0.65 ± 0.03	2.8±1.4									
SnCl₄	-25	138	0	31	2.15				13			1.48	≈6.88			
				32	3.86				9			1.41	26.25			
				33	5.67				10			1.25	₹4.91	350		100
				34	7.38				10			1.22	≈4.68			
				35	7.38											
SF6	-44	62	0	36	1.42	0.280	5.67									
				37	2.02	0.306	5.49	36.0	43.1	0.845	0.28	0.785	0.74	180	5.4	60
				38	3.57	0.303	7.06	23.5	28.8	0.849	0.24	0.818	1.43			
				39	5.21	0.351	6.61	13.5	16.8	0.870	0.05	0.867	1.90			
				40	6.76	0.310	6.71	10.1	12.7	0.869	0.05	0.867	1.75			
					(Average)	$0.31 {\pm} 0.03$	6.3 ± 0.8									

TABLE III. Reactive systems. Parameters for exp-6 ($\alpha = 12$) potential, threshold energies and distances, and reaction cross sections.

* Standard energy change of reaction at absolute zero.

^o Based on Eq. (2) except for SnCl4 where we use Eq. (3).

^b See Footnote a, Table II.

^d Obtained from L, see Sec. VI.C.

^o C. G. Le Fèvre and R. J. W. Le Fèvre, J. Chem. Soc. 1954, 1577.

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correction is large and uncertain at small angles; at $\log x = 0.6$ approximately 0.1 should be added to the points. The correction decreases with increasing χ and becomes negligible by $\log \chi = 0.8$. It is seen that there is a change in slope at about $\chi = 10^{\circ} (\log \chi \sim 1.0)$. The small-angle scattering is roughly that predicted for a potential V(r) varying as r^{-6} with the approximation for the cross section at small scattering angles [Ref. 10, Eq. (II.6')]. The change in slope at $\chi \approx 10^{\circ}$ cannot be due to a change in potential without the occurrence of chemical reaction, because the observed scattering pattern shows neither rainbow scattering, expected for kinetic energies above a critical value depending on the potential, nor the scattering predicted for kinetic energies below the critical value where orbiting is possible (Ref. 5, p. 164). Hence, we take the changes in slope to be evidence of chemical reaction thresholds. Moreover, there is some indication, as we see shortly, that the scattering to angles larger than the threshold angles is in part determined by a potential considerably different from the r^{-6} van der Waals attraction.

We do not know the parameters in the interaction potential for the small-angle scattering of K+SnCl₄. A reasonable guess based on a comparison with K+CCl₄ and K+SiCl₄ (Table III) is $\epsilon = 0.7$ kcal/mole, $r_m = 5$ Å. Using these values we can calculate reduced impact parameters, $\beta_{\rm thr}$ at these changes in slope, and from these in turn upper limits to the total reaction cross section

$$\frac{\sigma_R(\bar{E})}{r_m^2} = 2\pi \int_0^{\beta \text{ thr}} P(\bar{E},\beta)\beta d\beta, \qquad (2)$$

$$\sigma_R(\bar{E}) \leq \pi r_m^2 \beta_{\rm thr}^2. \tag{3}$$

We guess that the probability of reaction becomes nearly unity as the impact parameter becomes smaller than its threshold value so that the upper limit on the reaction cross section is likely to be a good approximation to the actual cross section.

Finally, the following argument gives an indication that the form of the potential of interaction for the nonreactive scattering of K may change at the threshold. Suppose we assume that such a change does not occur, and also that the reaction probability, with its threshold at $\beta \approx 1.3$, is nearly unity for the much smaller reduced impact parameters corresponding to the positive branch of the classical deflection function $\chi(\beta, K)$. Then no elastic scattering of K is predicted for angles larger than the rainbow angle, the maximum negative angle of the deflection function. However, the rainbow angles calculated with the assumed potential parameters are smaller than the angles at which scattering is observed (for the three largest relative kinetic energies), and hence a change in potential at threshold is likely. This argument, as well as Eq. (1) does not hold if the reactive channels influence the elastic scattering potential significantly.

B. Total Reaction Cross Section from Probability of Reaction

The calculated values of the reduced total reaction cross section as given by Eq. (2) are listed in Table III for the systems $K+CH_{3}I$, CCl_{4} , and SF_{6} , together with the upper limits on σ_{R}/r_{m}^{2} for $K+SnCl_{4}$ obtained according to Eq. (3).

VI. COMPARISON WITH OTHER WORK

A. Potential Parameters

The only previous measurements with which the present results can be compared are on $K+CCl_4$ ¹¹ and on $K+CH_3I^2$. The two sets of experiments seem to be consistent, but potential parameters were not reported in Ref. 11. The consistency may be tested for K+CCl₄ by using the van der Waals constant C reported in Ref. 11 and our value of ϵ to obtain a value of r_m from the relation $C = 2\epsilon r_m^6$ which holds for our assumed potential. This gives $r_m = 5.4$ Å which is in good agreement with our value $r_m = 5.5 \pm 1.8$ Å in Table III. In Ref. 2, differential scattering cross sections were presented for the scattering of Na by CH₃I but only potential parameters [Lennard-Jones (8, 6)] were listed for K+ CH₃I. Although the parameters given by the authors $(\epsilon = 0.336 \text{ kcal/mole}, r_m = 8.0 \text{ Å})$ differ from those in Table III, the difference is apparently due not so much to a difference in the measured differential cross section as to our locating the rainbow angle further from the maximum.

The values of the potential parameter ϵ for K+ C(CH₃)₄ in Table III are higher by 20% than those reported previously.⁵

The original work⁵ was reproduced once (within 1.5%) but in the work reported here, Runs 1-6, the large difference appeared. Hence the measurements were repeated¹² once more and results were found identical (within 2%) to those leading to the ϵ 's listed in Table III. A mass-spectrometric and an infrared analysis made of the neopentane used for the last two determinations confirmed the identity and purity of this sample. The reason for this discrepancy, which is considerably outside the limit of the estimated accuracy, is not known.

B. Total Reaction Cross Sections

The total reaction cross section of $K+CH_3I$ ranges from 25 to 47 Å² for the range of relative energy of the present measurements. To obtain these values we take the size parameter r_m to be 4.8 Å, a number obtained

¹¹ R. Helbing and H. Pauly, Z. Physik 179, 16 (1964).

¹² E. F. Greene, L. Hoffman, M. W. Lee, and J. Ross (unpublished results).

¹⁰ R. B. Bernstein, Advan. Chem. Phys. 10, 75 (1966).

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				М	Threshol lodel	Threshold distances Nonreactive	
MY_mX_n	ΔE_0° (kcal/mole)	$-\Delta E_0^{\circ}/D_e(\mathbf{KX})$		* KX (Å)	$r_{KX} + r_c$ (Å)	уг _т (Å)	
SiCl4	(-14)	0.14	$\begin{array}{c} (E_a \leq 0) \\ (E_a > 0) \end{array}$	<3.26 <2.67	<5.28 <4.69	(2.5)	(R)
SF ₆	(-44)	0.38		3.30	4.88	$ \begin{cases} 5.3 - 5.5 \\ 4.6 - 4.7 \end{cases} $	(R) (L)
CCl ₄	(-31)	0.31		3.70	5.47	$ \begin{cases} 4.8 - 4.9 \\ 4.0 - 4.1 \end{cases} $	(R) (L)
SnCl ₄	(-25)	0.25		3.55	5.85	6.1	(G)
HCl	1	0.01		2.67	2.71	2.8	(R)b
HBr	4	0.04		3.12	3.14	3.6	(R+K)
HI	-6	0.08		3.50	3.51	3.4	(R) ^b
CH₃Br	(-23)	0.26		3.77	4.08	5.0-5.1	(L) ^b
CH₃I	(-22)	0.29		4.14	4.38	4.1-4.2	(L)

TABLE IV. Comparison of threshold distances obtained from nonreactive scattering and from a simple model for reactions $K + MY_m X_n \rightarrow KX + MY_m X_{n-1}$.

^a ΔE_0° , standard energy change for reaction at 0°K; $D_e(KX)$, dissociation energy of KX; r_{KX} , outer ($E_a \leq 0$) or inner ($E_a > 0$) turning point of Morse potential for energy ΔE_0° ; r_c , distance from Atom X to center of mass of MY_mX_n ; yr_m , threshold distance with r_m determined from rainbow scattering (R), kinematics (K), by the method of Sec. VI.C (L), or by a guess based on discussion in Sec. V.A (G). Energies, bond distances, and vibration frequencies: for KX from L. Brewer and E. Brackett, Chem. Rev. 61, 425 (1961); for HX from G. Herzberg Spectra of Diatomic Molecules (D. Van Nostrand Co., Inc.,

N. J., 1950), 2nd ed.; for polyatomic molecules from T. L. Cottrell The Strengths of Chemical Bonds (Butterworths Scientific Publications, Ltd., London, 1958) and Landolt-Börnstein Zahlenwerte und Funktionen. A. M. Hellwege and K. H. Hellwege, Eds. (Springer-Verlag, Berlin, 1951), Vol. 1, Part 2. Values of ΔE_{0} in parentheses are obtained from heats of atomization and are therefore less certain. ^b Reference 5.

^c Reference 8.

from a comparison of the experiments with an opticalmodel calculation (see below). The magnitude of r_m seems reasonable compared to K+HI for which r_m is 3.9 Å.⁵ The total reaction cross section deduced for K+CH₃I is also quite similar to that reported for K+CH₃Br.⁵

From measurements on reaction yield¹³ the total reaction cross section is found to be 35 Å and the product appears predominantly at large scattering angles ($\chi \approx 180^\circ$). Although both measurements are made in molecular-beam experiments, the methods are quite different and, in view of the uncertainties, the agreement between them is remarkable.

Raff and Karplus¹⁴ have made a classical calculation of the reaction dynamics for K+CH₃I. They used a number of assumed potential energy surfaces and a relative energy of 1.44 kcal/mole. Their values of the total cross section range from 13.1 to 36.1 Å,² depending on the potential surface. In Fig. 12 we compare their calculation of the probability of reaction with the same quantity derived from our interpretation. The agreement seems reasonable.

For a series of compounds, including M (alkali metal)+CCl₄, SiCl₄, SnCl₄, and SF₆, the Harvard group¹ has made measurements of the angular distri-



FIG. 12. K+CH₃I, probability of reaction vs re-duced impact parameter for several relative energies, in kcal/mole. The solid lines are classical calcula-tions for three potential surfaces (Ref. 14).

¹⁸ D. R. Herschbach, G. H. Kwei, and J. A. Norris, J. Chem. Phys. **34**, 1842 (1961). D. R. Herschbach, Ref. 1, reports that recent measurements on the reaction yield correspond to a total cross section of ~ 35 Å².

¹⁴ L. M. Raff and M. Karplus, J. Chem. Phys. 44, 1212 (1966).

bution and yield of product MX which show that SiCl₄ is nearly unreactive (see also Sec. C, below), while SnCl₄ and SF₆ give a large yield of product $(\sigma_R \ge 100 \text{ Å}^2)$ which appears predominantly at small scattering angles ($\chi \approx 0^{\circ}$). CCl₄ gives reaction yields and angular distributions intermediate between the two extremes represented by CH₃I and SnCl₄. These trends, as well as the group's measurements of the nonreactive scattering of M in thermal molecular beams, are consistent with the present measurements. Herschbach notes that for these reactions, increased yields can be correlated with a shift of the angular distribution of the product to smaller relative scattering angles. Not surprisingly, we find that the reduced threshold impact parameters, which we infer from our measurements, increase as the product distribution moves from backward to forward scattering. The only exception is SF₆ where the reduced threshold impact parameters are no larger than those for CH₃I, even though KF is reported to be scattered predominantly forward.

C. Optical-Model Calculations

Hundhausen and Pauly² have made a calculation of the elastic scattering in a system in which the quantummechanical phase shifts are taken to be real for large values of the orbital angular momentum quantum number l, $l \ge L$, but pure imaginary for l < L, where L is a cutoff parameter. They evaluated the real phase shifts by the WKB method for a Lennard-Jones potential (8, 6), for one reduced energy $K = E/\epsilon = 8.4$, and one size parameter $r_m = 5.2$ Å, but for a number of values of L. The results of this calculation are given in Fig. 10 of their paper.

A qualitative comparison of our experiments with these calculations at approximately the same energy leads to estimates of L, the threshold angular-momentum quantum numbers, which are listed in Table III. If we combine these estimates of L in the semiclassical limit $L\hbar = \mu v \beta r_m$ with reduced threshold impact parameters calculated in Sec. V.A we obtain an independent evaluation of the potential parameter r_m , Table III. The total reaction cross section in this simple optical model is $\sigma_R = \pi L^2 \hbar^2 / 2\mu E$, and the values so calculated are also listed in Table III. Although the optical model with a sharp cutoff may be too severe an

approximation, it provides a useful comparison with the measurements.15

The large-angle scattering for a number of systems shows variations in amplitude which in the case of SiCl₄ (E = 3.36 kcal/mole) are larger than our estimate of the noise level. These variations appear to be similar to those in the curve for L=150 in Fig. 10 of Ref. 2, An optical-model calculation made with the stationary phase method¹⁶ yields a threshold L of 63, Table III. The total reaction cross section derived from this L is considerably smaller than those for the other systems.

D. Spectator Model

The threshold distances determined from the nonreactive scattering (Table III) may be compared with threshold distances estimated on the basis of the following very simple model.⁴ Reaction is assumed to occur whenever the approaching K atom comes within a particular distance. For an endothermic reaction $(\Delta E_0^{\circ} > 0)$ or one with an activation energy (E_a) this distance (r_{KX}) is taken as the inner turning point of a Morse potential for KX. The threshold potential energy is just that needed to satisfy $V(y) = \Delta E_0^{\circ}$ or E_a . For an exothermic reaction, all the ΔE_0° is assumed to be converted into vibrational energy of KX and then the corresponding outer turning point of KX is taken for $r_{\rm KX}$. For comparison with the threshold distances (yr_m) the distance from Atom X to the center of mass of the halide molecule is added to $r_{\rm KX}$. During the whole reaction the presence of the remainder of the original halide molecule is ignored; it is taken to be a noninteracting spectator. As Table IV shows there is reasonable agreement for all the compounds (including some reported earlier) except SiCl₄, where we found what seems to be an unreasonably small value of r_m .

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¹⁵ Since Hundhausen and Pauly² used a particular value for the size parameter $(r_m = 5.2 \text{ Å})$ in their calculations, these are not strictly comparable with our experiments which yield a range of r_m . We assume that this discrepancy in r_m does not affect our estimate of L and the r_m derived from it. ¹⁶ H. Y. Sun and J. Ross, J. Chem. Phys. 46, 3306 (1967).