

Translational Energy Dependence of Product Energy and Angular Distribution for the $K + CH_3I$ Reaction *

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Molecular beam scattering (velocity-analysis) experiments have been carried out for the now-classic "rebound" reaction $K + CH_3I \rightarrow KI + CH_3$ over a range of relative translational energies E_T from 0.077 to 0.16 eV. Detailed centre-of-mass differential reaction cross sections have thereby been obtained (at three energies), showing the expected predominant "back-scattering" of the fast-recoiling KI product. There is very little coupling between the angular and recoil energy distributions. The differential solid-angle cross section peaks at 180° (with a half-angle close to 90°) with shape essentially independent of E_T over the range of the experiments. The distribution of final translational energy $E_{T'}$ is rather sharp, showing a peak at about 60 % of the total available energy. The average recoil energy $\bar{E}_{T'}$ increases with E_T .

These results are combined with previous experimental findings from this laboratory on the CH_3I-K , $-Rb$ reactions (the "alignment effect" and the E_T -dependence of the total reaction cross section), and compared with observations of other groups. A current, overall, experimental summary is presented, to serve as a target for theory.

The molecular beam reaction of potassium with methyl iodide is the prototype "rebound" reaction.¹ For a dozen years of the "alkali age" ² this and closely related reactions have been a source of essentially continuous inspiration (or at least continuous publication), more than thirty experimental and/or theoretical-computational reports having by now appeared in print. Most of them are referred to in our own most recent experimental article,³ which forms the basis of much of what follows. An excellent prior review is now five years of age.⁴

By way of background, the reaction is believed to be of the "impulsive" type, with considerable "repulsive energy release".⁵ Since the geometry of the leaving group, CH_3 , changes from pyramidal to planar in the course of the reaction there is the possibility of considerable vibrational excitation of the CH_3 . Information on this question comes from a photofragmentation study of CH_3I .⁶ It was found that, although a large fraction ($\approx 85\%$) of the *ca.* 2.5 eV total available energy E appears as relative translation ($E_{T'}$) of the $I \dots CH_3$, still a significant amount remains as internal excitation of the CH_3 . For the reaction with potassium the partitioning of the *ca.* 1 eV of exoergicity into relative translation of the $(KI \dots CH_3)$ versus overall product internal excitation is now known,³ but the degree of excitation of the CH_3 relative to that of the KI is still very uncertain.

Although there has never been much doubt about the dominant "back-scattering" feature of the angular distribution of the KI, there has been difficulty in establishing the product centre-of-mass (c.m.) recoil energy distribution function $P(E_{T'})$ or $d\sigma/dE_{T'}$ (mainly because of awkward kinematics). The experiments of ref. (3) employed velocity selection of the K beam, which allowed resolution (in velocity

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space) of the KI product from the non-reactive scattered K and, of course, made it possible to study the E_T -dependence of the detailed differential cross section

$$d^3\sigma(\theta, E_T | E_T)/d^2\omega dE_T.$$

With another apparatus employing a seeded supersonic beam of CH_3I crossed by a thermal K beam it has been possible to measure the overall E_T -dependence of the reaction cross section, $\sigma(E_T)$, from 0.1 to 1 eV.⁷

The appearance of a rather pronounced maximum in the cross section near 0.18 eV has given renewed impetus to Monte Carlo trajectory investigations^{8,9} of this and related systems. The attempt is to find a potential energy surface which could induce this behaviour (as well as reproduce the alignment effect and the gross features of the angular and recoil energy distributions). These third or fourth-generation semi-empirical studies (descendants of the first such attempt for this reaction, in 1962¹⁰) have not yet come close to a satisfactory rendition of the observed chemical dynamics. However, the experimental picture itself has been a long time in taking firm shape; it is hoped that the summary which follows will be a useful base of reference for future theoretical-computational efforts.

RECENT EXPERIMENTAL RESULTS

DETAILED DIFFERENTIAL REACTION CROSS SECTIONS AND THE ANGULAR DISTRIBUTION

Fig. 1 shows a simplified c.m. flux-velocity-angle contour map¹¹ for the KI product (for an intermediate value of the relative translational energy, $\bar{E}_T = 0.12_1$ eV), from ref. (3). The contours represent the detailed differential reaction cross section $d^3\sigma(\theta, w')/d^2\omega dw'$, where θ is the angle of scattering of the KI with respect to the

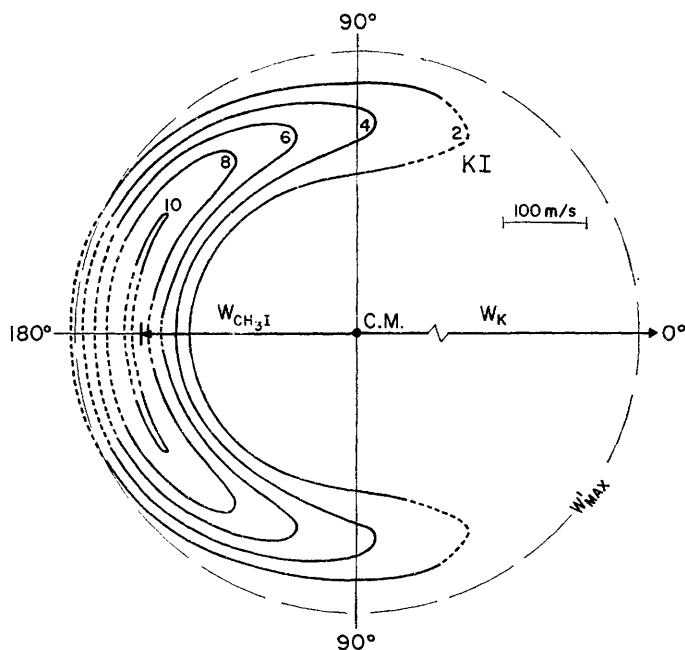


FIG. 1.—KI polar (c.m.) contour map, i.e., detailed differential cross section for the $\text{K} + \text{CH}_3\text{I}$ reaction at $\bar{E}_T = 0.12$ eV; for details, see ref. (3). Dashed contours less reliable. Outer dashed circle denotes nominal maximum KI recoil velocity (from energy conservation).

incident K velocity and w' the recoil velocity of the KI with respect to the c.m. The dashed circle represents the nominal energy-conservation limit of w' . The near-circular contour lines imply that the angular-recoil velocity distributions are nearly "uncoupled".

Integration at a given θ over all recoil velocities yields the differential (solid-angle) reaction cross section, $d^2\sigma(\theta)/d^2\omega$, shown in a polar coordinate representation in fig. 2. The peak is at 180° , and the angle at which it drops to half its peak value is $H_4 \cong 90^\circ$. In ref. (3) it was shown that the shape of this "angular distribution" is essentially independent of \bar{E}_T over the range studied (0.077 to 0.16 eV).

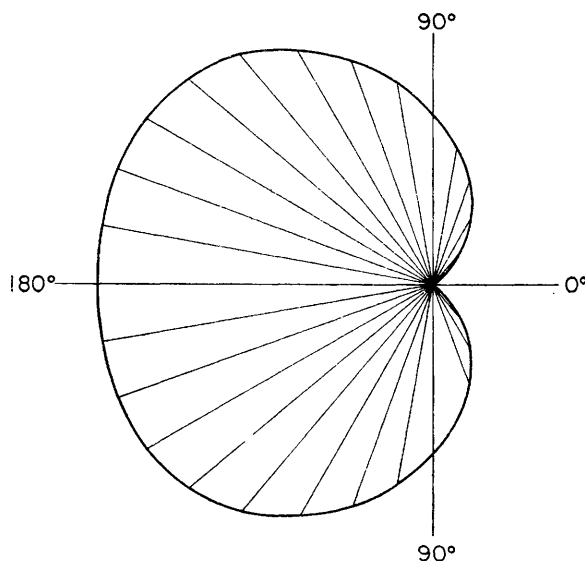


FIG. 2.—Polar coordinate plot of the c.m. angular distribution of KI, essentially independent of \bar{E}_T over the thermal range. From data of ref. (3).

RECOIL DISTRIBUTION FUNCTIONS

Integration at given w' (or E_T) over all angles yields (after some manipulation)³ the c.m. translational energy distribution function $d\sigma/dE_T$ as shown in fig. 3. (Since absolute cross sections are rarely available, such curves, designated $P(E')$, are usually scaled arbitrarily.)

There is seen to be a significant trend, i.e., a shift of the whole product translational energy distribution to higher energies for increasing reactant translational energy. The average value of E_T , i.e., \bar{E}_T , was found to vary from 0.65 to 0.76 eV as \bar{E}_T was increased from 0.077 to 0.161 eV, so that $d\bar{E}_T/d\bar{E}_T \approx 1.3$ (over this limited range of \bar{E}_T).

A qualitatively similar trend was reported for the $D + I_2$ reaction.¹² The most accurate manifestation of this effect comes from the chemiluminescence study of the $Cl + HI$ reaction,¹³ for which $d\bar{E}_T/d\bar{E}_T$ was found to be 0.9. The results show that E_T can be "efficiently converted" into \bar{E}_T .

MISCELLANEOUS RECENT OBSERVATIONS

During the detailed investigation³ of the reactive scattering (of KI from $K + CH_3I$) a concomitant study was carried out of the non-reactive scattering of the K.¹⁴

A preliminary analysis of the velocity and angular distribution results indicated the presence of a substantial inelastic component, mainly rotational excitation. Both the angular distribution of the inelasticity and its energy dependence were observed (over the limited E_T -range of the study). A more extensive treatment of the data is required¹⁵ to yield the c.m. probability density function for the inelasticity (at least the first and second moments¹⁶ of the energy transfer function).

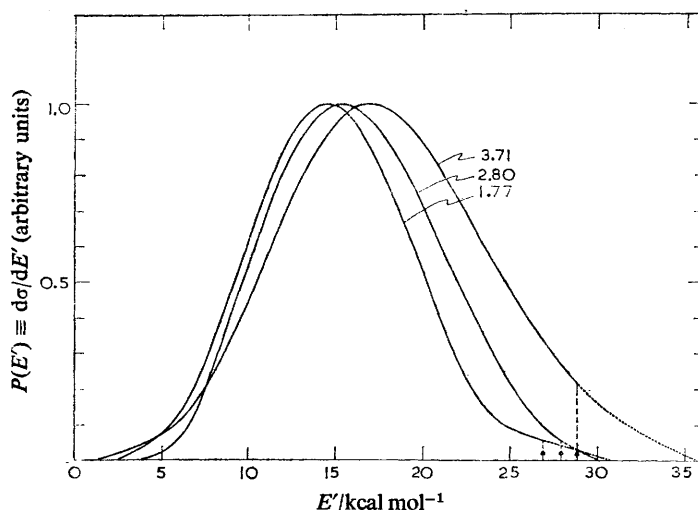


FIG. 3.—Product recoil energy distribution $P(E')$ for the three values of the initial translation energy, $\bar{E}_T = 0.077, 0.121$ and 0.160 eV, labelled in this figure as 1.77, 2.80 and 3.71 kcal mol⁻¹ respectively.³ Vertical arrows denote the nominal conservation-limited value of the available energy. Dashed “tails” of the distributions are believed to be spurious.³

At the present time, all that can be said is that the inelasticity concurrent with the reaction is significant; but it is probably far less extensive than that observed recently¹⁷ for the non-reactive Ar-CsI system (at higher E_T , but below the threshold for dissociation).

One additional piece of (fragmentary) information was obtained from our recent study^{3, 14} regarding the partitioning of the internal excitation energy between the two product molecules KI and CH₃. Using the vibrational-excitation-sensitive surface ionization detector¹⁸ it was found that the KI was highly excited,¹⁹ implying by difference that the CH₃ is internally rather “cold”.

SUMMARY OF EXPERIMENTAL FINDINGS ON THE REACTIVE SCATTERING

This summary deals only with experiments in which neutral products (e.g., KI) have been observed. Thus it does not cover the non-reactive (e.g., rainbow) scattering experiments from which information on the reaction probability can be gleaned via opacity analysis, nor does it consider collisional ionization experiments. Naturally, it also omits mention of dynamical model calculations and trajectory studies of potential surfaces. The summary is presented as a series of succinct statements attempting to represent the experimental facts. (References are not given; most have been cited in ref. 3 and/or a recent general review.²⁰) Each statement is accompanied by a (highly subjective!) appraisal of the % confidence level (C.L.)

of the statement. (Thus the summary is intended also as a prototype of a semi-quantitative rating system for similar well-studied systems.) The following conventions were adopted: (i) no statement will be listed unless its C.L. $\geq 50\%$, (ii) any statement based upon only a single experimental study (i.e., unconfirmed by an

TABLE 1.—SUMMARY OF EXPERIMENTAL FINDINGS ON THE REACTIVE SCATTERING OF $K + CH_3I$

| no. | range of E_T /eV | statement of experimental result | confidence level (C.L., %) |
|-----|--------------------|---|-------------------------------|
| 1 | — | zero-point exoergicity, $-\Delta E_0 = 1.1 \pm 0.1_5$ eV | >95 |
| 2 | ≈ 0.15 | rebound reaction; KI predominantly scattered into "backward" (c.m.) hemisphere | >95 |
| 3 | ≈ 0.15 | extensive translational recoil: $\bar{E}_T \gtrsim$ half of the total available energy | 90 |
| 4 | ≈ 0.15 | maximum in $d^2\sigma(\theta)/d^2\omega$ at $160^\circ \leq \theta \leq 180^\circ$ | 90 |
| 5 | ≈ 0.15 | total reaction cross section σ increases from low E_T (toward a maximum) | 85 |
| 6 | ≈ 0.1 | reactive asymmetry; alignment effect factor $\lesssim 2$ in back-scattering ($\lesssim 3$ for Rb reaction) | 85 |
| 7 | ≈ 0.15 | breadth of c.m. angular distribution: $H_{\frac{1}{2}} = 90^\circ \pm 10^\circ$ | 80 |
| 8 | ≈ 0.15 | angular and recoil distributions nearly "uncoupled", i.e., factorizable, within <i>ca.</i> $\pm 25\%$ | 75 |
| 9 | ≈ 0.15 | $E'_{m.p.} \cong \bar{E}_T = 0.7 \pm 0.1$ eV | 75 |
| 10 | 0.1-1.0 | maximum in σ at $E_T = 0.18 \pm 0.04$ eV | 75 |
| 11 | 0.5-1.0 | negligible competing reaction: $\sigma(KCH_3)/\sigma(KI) \approx 0.05$ | 70 |
| 12 | ≈ 0.15 | increase in \bar{E}_T with E_T : $d\bar{E}_T/dE_T \approx 1$ | 70 |
| 13 | ≈ 0.15 | absolute reaction cross section: 35 ± 15 Å ² | 65 |
| 14 | ≈ 0.15 | $E'_{int}(KI) = 0.5 \pm 0.2_5$ eV | 60 |
| 15 | ≈ 0.15 | $E'_{int}(CH_3) \approx 0.2$ eV | 50 |

independent investigation) will not receive a C.L. in excess of 75 %. Due to the uncertainty in estimating C.L. values, specification to better than $\pm 5\%$ C.L. will not be attempted. Rather than arranging the list in the obvious order of logically related observations, the statements are placed in a hierarchical descending order of certainty (i.e., C.L.), to facilitate comparison with theory. (Of course, the sequence and the C.L. ratings will drastically change when new experimental results become available.) Table 1 thus represents a summary of the present status of experimental findings.

CONCLUDING REMARKS

Table 1 should serve as a "profile" of the experimental behaviour of the well-studied crossed-beam reaction $K + CH_3I \rightarrow KI + CH_3$. However, much remains to be done to confirm the picture. There has not yet been a satisfactory correlation between the reactive and the non-reactive (elastic and inelastic) scattering results, even at thermal energies. There has been insufficient experimentation in the epithermal region. The E_T -dependence of the product angular and translational energy distribution is essential dynamical information. Experiments should be extended to 2 eV at least (the threshold for collision-induced dissociation). A knowledge of the influence of internal excitation of the CH_3I upon the cross section at low energies would be of great importance. The questions of energy disposal and energy requirements (of specificity of the energy release and selectivity of the energy requirements) are of considerable theoretical interest.²¹ The extent to which the observed dynamical behaviour depends upon the polyatomic character of the methyl radical

is still unknown; detailed experiments for $K + CD_3I$ (and C_2H_5I) would be illuminating. "Comparative anatomy" studies (among different alkalis and alkaline earths, and comparing $K + CF_3I$, CH_3Br , etc.) have thus far been only fragmentary in nature, and should be dealt with seriously in the near future. However, even without further experimental knowledge the picture provided by table 1 is sufficiently detailed that it has become almost *too* restrictive as a characterization of this reaction. We have now reached the position where none of the previously reasonable dynamical models or trajectory calculations comes close to producing an acceptable simulation of the overall experimental results!

We can hope, however, that in the next few years we shall see a convergence between our experimental knowledge and our theoretical understanding of the reaction dynamics.

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