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tions, the rotational viscosity of the ester is too large (3.3 P at $t_r = 0.98$) to allow its practical application as a major component in a standard twisted nematic display cf. the rotational viscosity of *trans*-1-(4-cyanophenyl)-4-heptylcyclohexane, one homolog of a class of nematic liquid crystals found in many commercial mixtures, is much lower, i.e., 1.5 P at 25 °C). However, the value of this ester as an additive to lower the threshold voltage of a given nematic mixture is demonstrated by the fact that adding 10 wt. % of the ester to a commercial mixture (ZLI1957/5 of Merck) markedly decreases the threshold voltage (1.8 to 1.4 V) and causes only a small decrease (~5 °C) in the nematic-isotropic transition temperature, while the steepness of the electrooptic curve remains almost unchanged.

4-Cyano-3-fluorophenyl 4-heptylbenzoate is a terminally cyano-substituted liquid crystal, which exhibits a nematic phase of outstandingly high positive dielectric anisotropy and no short-range molecular association. It appears that the fluorine atom next to the cyano-group prevents the association of nearest neighbor molecules. Due to the magnitude of their dielectric anisotropy, members of this class of compound can be used in relatively low concentrations in nematic mixtures to significantly lower the threshold voltage.

¹M. Schadt and W. Helfrich, Appl. Phys. Lett. 18, 127 (1971).

- ²A. J. Leadbetter, R. M. Richardson, and C. N. Colling, J. Phys. (Paris) Colloq. **36**, 37 (1975).
- ³Hp. Schad and M. A. Osman, J. Chem. Phys. **75**, 880 (1981), and references therein.

⁴Hp. Schad and M. A. Osman, J. Chem. Phys. 79, 5710 (1983).

⁵S. M. Kelly, Helv. Chim. Acta (in press).

⁶Hp. Schad and S. M. Kelly (to be published).

Translational energy of products in the $K + CH_3COCI \rightarrow KCI + CH_3CO$ reaction^{a)}

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Reactions of alkali metals with alkyl halides have been studied extensively in crossed molecular beams.¹⁻⁴ On the contrary, reactions with acetyl halides have received much less attention, although these compounds are more reactive with alkali metals than the alkyl halides.⁵ Goldbaum and Martin⁶ have reported on a crossed beam study with effusive beam sources, but were only able to deduce total cross-sections. In this note, we present measurements of the products' translational energy of the title reaction at two initial translational energies. The results will be compared with simple models. The apparatus and general experimental procedure have been described elsewhere.7 Nozzle beams of K seeded with Ar or He and pure CH₃COCl are crossed at right angles and the velocity distribution of scattered K and KCl is measured by the pseudorandom time-of-flight (TOF) technique at various laboratory angles. Care was exercised to avoid hydrolysis of the acetyl chloride by moisture. Before use, the chloride was distilled and sealed off into glass ampoules that were broken under inert gas atmosphere just prior to the start of an experimental run. The absence of HCl in the beam was ascertained by mass spectral analysis. The important experimental parameters of the beams are given in Table I. Because of unfavorable signal-to-noise ratios, TOF distributions could not be measured over the full angular range. Furthermore, the distributions of nonreactive K and reactive KCl appreciably overlap, but the maxima of both contributions could be resolved. A complete inversion of the laboratory data to the center-of-mass (c.m.) system is therefore impossible. Figure 1 in the upper part shows measured TOF distributions at three laboratory angles for the lower collision energy. The first peak at smaller flight time is due to K and the second to KCl. Similar results were obtained over

TABLE I. Experimental conditions.

Most probable velocity (m/s)	Speed ratio
960	10.2
2203	10.3
550	3.6
Mean collision energy (eV)	
0.16	
0.70	
	Most probable velocity (m/s) 960 2203 550 Mean collision energy 0.16 0.70

the angular range $30-50^{\circ}$ at the higher collision energy. Despite the incompleteness of the data, the mean translational energy of the products can be obtained by making a number of simplifying assumptions about the form of the c.m. cross-section. It was assumed that the c.m. cross section is separable in angle and velocity and can be written as the product of two Gaussian functions:

$$I_{\text{c.m.}}(\vartheta, w) \sim \exp\{-\ln 2[(\vartheta - \vartheta_0)/\Delta\vartheta]^2\} \times \exp\{-\left[\left(\frac{w}{w_0} - 1\right)/\beta\right]^2\},\$$

where ϑ_0 and w_0 denote the peaks of the two distributions and $\Delta \vartheta$ and β are parameters for the respective widths. This or similar forms of $I_{c.m.}(\vartheta, w)$ have been quite successful for M + RX (R = alkyl) systems. Fully averaged laboratory angular distributions were calculated by the method outlined in Ref. 8 for various combinations of the four parameters of the c.m. function and compared to the experimental distributions. These calculations revealed that the maxima of the

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 $K (Ar) + CH_{3}COCL$

FIG. 1. Measured and calculated laboratory TOF distributions at 0.16 eV collision energy. The first large peak in the measured distributions is unreactively scattered K.

KCl TOF distributions depend very sensitively on w_0 and much less on the other parameters. This can be seen in the lower part of Fig. 1, where calculated distributions are displayed for three values of the products mean translational energy \overline{E}'_{T} .⁹ The c.m. parameters that best match the maxima of the experimental TOF distributions are given in Table II. Here only \overline{E}'_{T} was actually fitted, whereas reasonable ranges were explored for the other parameters. From Ref. 6, a broad rebound c.m. angular distribution is suggested, which led to the parameters of ϑ_0 and $\Delta \vartheta$ in Table II. The β values were chosen to approximately reproduce the width of the TOF distributions, but no great precision is claimed. Compared to the results obtained for the M + RX systems, the translational energy of the products of $K + CH_3COCl$ is surprisingly low. The exothermicity of the reaction of $\sim 1 \text{ eV}$ is mainly converted into internal energy of the products. An increase of the initial kinetic energy, however, results also in additional translational energy of the products as found for all M + RX systems studied. The most successful model conception of energy disposal at low energies for the M + RX reactions is the photodissociation model of Herschbach,² which will now be applied to the present reaction. This model yields $\overline{E}'_{T,0} = (\mu_{\rm CO,Cl}/\mu_{\rm CH,CO,KCl}) \cdot R_0$ for

TABLE II. Best fit c.m. parameters.

	$\overline{E}_T = 0.16 \text{ eV}$	$\overline{E}_T = 0.70 \text{ eV}$
$\vartheta_0[deg]$	180	180
$\Delta \vartheta [deg]$	140	140
$\overline{E}'_{T}[eV]$	0.069	0.48
β	0.35	0.45

the products translational energy at $E_T = 0$. The μ 's are reduced masses and R_0 is the difference between the electron affinity of chlorine¹⁰ and the dissociation energy of the carbon-chlorine bond in CH₃COCl¹⁰, giving $R_0 = 0.1$ eV. Together with the mass factor, this yields a value of 0.06 eV for $\overline{E}_{T,0}$. A low translational energy of the products in the limit of $E_T = 0$ is thus predicted by the model in qualitative accord with the experiment. The energy dependence of \overline{E}_T' can be estimated from the two points as $\Delta \overline{E}_T'/\Delta E_T \simeq 0.7$, comparable in magnitude to M + RX systems.¹¹

This and the previous work^{5,6} has shown that CH_3COCl reacts with K more readily than CH_3Cl that is too unreactive to be studied in crossed beams.³ The increased reactivity is due to the presence of the electronegative C–O group stabilizing the negative molecular ion that results from the initial electron jump. In contrast to the reactions with alkyl halides, only a small amount of the available energy is channeled into product translation at low collision energy. This difference can be rationalized by the impulsive photodissociation model of Herschbach,² which predicts a much lower repulsive energy release for this system. At higher collision energy, the products' translational energy increases as for the alkyl halide systems.

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- ¹A. M. Rulis and R. B. Bernstein, J. Chem. Phys. 55, 5497 (1972).
- ²D. R. Herschbach, Faraday Discuss. Chem. Soc. 55, 233 (1973).
- ³H. F. Pang, K. T. Wu, and R. B. Bernstein, J. Chem. Phys. 69, 5267 (1978).
- ⁴V. J. Herrero, F. L. Tabares, V. Saez Rabanos, F. J. Aoiz, and A. Gonzáles
- Urená, Mol. Phys. 44, 1239 (1981).
- ⁵E. Warhurst, Quart. Rev. 5, 44 (1951).
- ⁶R. H. Goldbaum and L. R. Martin, J. Chem. Phys. 62, 1181 (1975).
- ⁷M. Pauluth and G. Rotzoll, Z. Phys. Chem. NF, 136, 171 (1983).
- ⁸G. Rotzoll, Chem. Phys. Lett. 85, 478 (1982).
- ${}^{\circ}\overline{E}'_{T}$ is related to the cm velocity distribution function by $\overline{E}'_{T} = 1/2$ $(m_{\text{KCl}} \cdot m_{\text{KCl} + \text{CH},\text{CO}} / m_{\text{CH},\text{CO}}) \overline{w_{\text{KCl}}^{2}}$.
- ¹⁰CRC Handbook of Chemistry and Physics, 63rd ed. edited by R. C. Wearst, (CRC, Boca Raton, 1982).
- ¹¹E. Pollak and R. B. Bernstein, J. Chem. Phys. 70, 3995 (1979).