329. *Competitive Alkali-metal Flame Reactions. The Reactions of Sodium and Potassium Atoms with Alkyl Halides and Acetyl Chloride.*

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By analysis of the solid sodium or potassium halides produced by the reactions of sodium or potassium atoms with a radioactively labelled and an unlabelled organic halogen compound, relative rate constants have been obtained for pairs of these reactions. The procedure has been repeated over a range of temperatures to give the activation energy differences and ratios of *A*-factors shown below.

Reactions of sodium atoms:

Reactant (1)	Reactant (2)	E_1–E_2 (cal.mole^{-1})	A_2/A_1	k_2/k_1 (at 285°)
MeCl	EtCl	608 ± 83	0·773 ± 0·060	1·33
MeI	MeCOCl	—	—	7·0

Reactions of potassium atoms:

Reactant (1)	Reactant (2)	$E_1 - E_2$ (cal.mole^{-1})	A_2/A_1	k_2/k_1
MeCl	EtCl	400 ± 90	0·83 ± 0·10	1·19
MeCl	MeCOCl	—	—	360
MeI	EtCl	—	—	38
MeI	MeCOCl	0	7·0	7·0
MeBr	MeCOCl	1400	3·5	12·6
MeBr	EtCl	4400	0·52	35

The results are considered in terms of the semi-empirical method of Eyring and Polanyi [1] and of the transition-state theory.

Although the reactions of alkali-metal atoms with halogen compounds have been extensively studied, few Arrhenius parameters are known for them. The dilute-flame and diffusion-flame methods devised by Polanyi and his co-workers,[1] and later adaptations, yield rate constants at a single temperature, but are not suitable for the measurement of temperature coefficients because of the difficulty of assessing the variation of quantities

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[1] Eyring and Polanyi, *Z. phys. Chem.*, 1931, *B*12, 279.

such as the diffusion coefficient and the limit of detectability of sodium atoms. We have applied the competitive method to the reactions of alkali-metal atoms with pairs of organic halogen compounds. By labelling one of the halides with chlorine-36 and by analysing for the total concentration and the concentration of radioactivity of the alkali metal, relative rate constants have been obtained. The procedure can be repeated at different temperatures because the immeasurable variables affect both reactions; hence relative Arrhenius parameters have been found.

EXPERIMENTAL

Apparatus for Experiments with Sodium Atoms.—The apparatus, as shown in Fig. 1, was constructed from Pyrex glass and was based on the classical design for the diffusion-flame technique with modifications for the removal of the sodium halide products. The sodium metal was contained in a stainless-steel boat (B) housed in a horizontal tube with a ground-glass joint for easy access. This tube was connected directly to the reaction vessel by means of a 3 mm. dia. nozzle. The sodium-saturator and reaction vessel were heated in three sections, marked I, II, and III, by wiring with nichrome wire lagged with asbestos string and paper. Temperatures were measured by means of thermocouples placed in wells (TW). The temperature of section II was kept at least 20° higher than that of section III. To obtain even heating in the reaction zone, a metal sheet was wrapped around the tubing before it was wired. The outside and inside thermocouples of the reaction vessel gave the same reading during a run, when placed at the same height. The temperature profile of the reaction zone, as measured by means of the outside thermocouple, showed a 6° hump along 10 cm. of the reaction zone, with the maximum opposite the jet. Power was supplied to the heating wire from a Variac connected to a mains stabiliser. The temperature of the reaction zone varied less than 1° during a run.

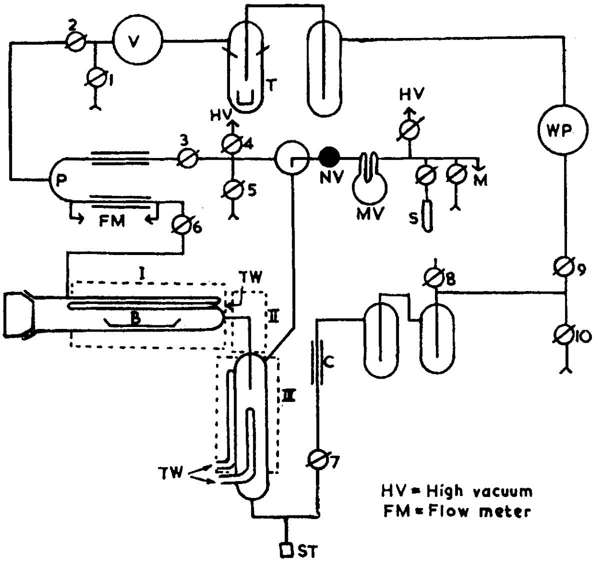

FIG. 1. Apparatus for experiments with sodium.

The carrier gas was oxygen-free nitrogen which was passed over sodium at 300° before entering a storage bulb, from which the desired amount, calculated from the pressure drop, was admitted to the circulating system. A Waran-type pump (WP), similar to that of Riemann,[2] produced a flow of *ca.* 40 c.c./sec. against a pressure of 10 mm. of mercury. The flow was regulated by means of a capillary (C), 8 cm. long and of 1·8 mm. dia. The rest of the flow-system consisted of a trap (T), containing sodium in a stainless-steel bucket to eliminate any

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[2] Riemann, " Vacuum Technique," Chapman and Hall, London, 1952.

remaining oxygen, a 2 l. bulb (V) to minimise fluctuations in the flow, and a branch-point (P) leading to two identical capillary tubes. One part of the flow was directed through the sodium-saturator and the other to the halide pick-up system.

The volume of the halide pick-up system was determined by weighing a known pressure of ethyl chloride. Mixtures of halides were made up in the usual way with the storage tube (S), the mixing vessel (MV), and the mercury manometer (M). Dead-space in the injection system was kept to a minimum by the use of capillary tubing. The amount of mixture introduced into the reaction vessel through a " Speedivac " needle-valve type LB1A (NV) was calculated from the pressure drop on the manometer. When the pressure of sodium, total pressure, and temperature of the reaction zone were fixed, the size of the flame was regulated by the pressure of the halide mixture. No appreciable absorption of the alkyl chlorides or bromides in the stopcock grease was observed, and with iodides and acetyl chloride, greaseless stopcocks were used throughout the halide injection system.

Procedure for Experiments with Sodium Atoms.—The sodium metal was kept for several hours in boiling toluene and fresh surfaces were cut just before it was introduced first into trap T under xylene. When the xylene had been pumped off, a vacuum was obtained, by use of stopcock 8, in the system between stopcocks 2 and 7 on the Waran-pump side. Trap T was heated until sodium appeared at the top, when stopcock 8 was closed and nitrogen carrier gas was introduced through stopcock 1. The sodium-boat was placed in the oven and a vacuum obtained in the remaining unevacuated part of the system as quickly as possible by use of stopcock 4. Sections II and III were heated and, with the pressure reduced to 5×10^{-5} mm. of mercury in the reactor system, the sodium oven was heated to a temperature of 140°. Carrier gas was then introduced, to reduce the diffusion of sodium vapour, and stopcocks 2 and 7 were closed to prevent circulation. When the temperature of the sodium-oven reached 190°, stopcock 6 was closed and 2 and 7 were opened. The flow of halides was then started and, after a few minutes, stopcock 6 was opened, in order to start the run. The temperature of the sodium continued to rise until it reached *ca.* 280°. For runs where it was necessary to keep the pressure ratio of halide to sodium at a known value, an excess of halide was used to avoid depletion at the end of a run, when the pressure of sodium was at its maximum. To end a run, the sodium-oven heater was shut off and, at a temperature of 190°, the flow of halide was stopped and stopcocks 2, 7, and 9 were closed. When the apparatus had cooled, air was admitted through stopcock 5 and the sodium-boat was taken out. To obtain a solution of the sodium halide, stopper ST was replaced by a standard joint attached to a stopcock, which in turn was attached to an open-ended cylinder by means of polyvinyl chloride tubing. The de-ionised water in this cylinder could then be admitted to the reaction vessel, by means of the stopcock, to a level controlled by the height of the cylinder. The water level inside the reaction zone usually reached 2 cm. above the mouth of the nozzle, and since the sodium-oven was kept closed at this stage, the water could not go far inside the jet. The water inside the reactor was collected and the process repeated, using, in all, about 60 c.c. of water. By opening the other end of the sodium-reactor, water was introduced into the inside of the jet. In this way sodium hydroxide was collected, but no sodium chloride could be detected. The bulk of the sodium chloride was obtained from the bottom of the reactor.

Apparatus for Experiments with Potassium Atoms.—From the experience gained with the sodium runs, the design of the potassium-reactor incorporated two features: (1) the use of the same potassium metal for several runs; and (2) collection of the solid product without introducing water into the vacuum system. The details are shown in Fig. 2. The potassium was kept in a stainless-steel bucket (B), under xylene when the system was not evacuated. The bucket was attached to an extension of the plug of stopcock 5 by a stainless-steel wire. Before the start of a run, the bucket was hoisted up out of the xylene, by turning stopcock 5, and directed into the vertical reactor by means of the glass hook H attached to a standard joint. Complete removal of the xylene from the potassium-bucket and degassing of the potassium were carried out in the usual way. To collect the solid products of the reaction, a glass cylinder (C), fitting closely to the walls, was placed inside the reactor. A small hole at the bottom of this collecting cylinder enabled the carrier gas to circulate, and a small piece of silicone tubing (ST), between the hole and the side-arm of the reactor, prevented carrier gas from diffusing between the tube and reactor. At the end of the run, the cylinder was removed and the solid products were dissolved in about 80 c.c. of water.

The heating system for the potassium-oven and -reactor consisted of vapour jackets of diethyl phthalate and mercury, respectively. The reactor temperature was varied between 220 and 360° by altering the pressure at which the mercury was boiled, and the diethyl phthalate was usually boiled at 400 mm. of mercury to give a potassium-oven temperature of 280°.

The remainder of the system was identical with that used for the experiments with sodium.

Procedure for Experiments with Potassium Atoms.—The method was essentially the same as that previously described for sodium. With nitrogen in the apparatus between stopcocks 2 and 7, and the sodium-trap for oxygen at 320°, the potassium was taken out of the xylene reservoir. The vapour jackets were then heated while the system was evacuated through stopcock 15. When steady temperatures were obtained in the potassium-oven and -reactor, stopcock 15 was closed, and the nitrogen carrier gas admitted with the circulating pump in operation. The flow of halides was started and, after a few minutes, the potassium-basket was lowered into the oven. At the end of a run, the potassium-heater was shut off, the basket raised, the mercury-heater shut off, the flow of halide stopped, and stopcocks 2 and 7 closed. Before the product was removed, the reactor was purged with nitrogen until the gas bubbled out of the mercury reservoir (R).

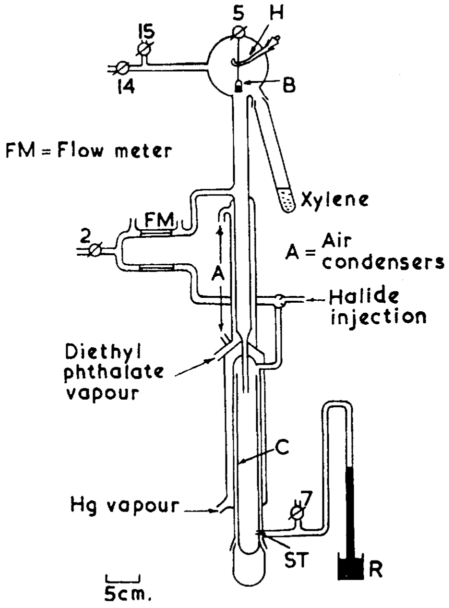

FIG. 2. Potassium-oven and -reactor.

Analysis.—(1) *Total* Cl^- *concentration.* The wash solution (*ca.* 80 c.c.) was concentrated (to *ca.* 1 c.c.) by evaporation, and weighed. About half the sample was reweighed, transferred to a small beaker with de-ionised water (30 c.c.), and the chloride concentration determined by a conductometric titration with a standard solution of silver nitrate. In some of the sodium runs the solution for analysis contained sodium hydroxide, and this was eliminated by adding dilute nitric acid dropwise until a sharp increase in conductivity was observed, before the solution was titrated with silver nitrate. The conductivity of the wash water was always checked before an analysis, usually in the same container.

(2) *Mixtures of* I^- *and* $^{36}Cl^-$, *or* Br^- *and* $^{36}Cl^-$. The total concentration of halide was again determined by conductometric titration with a standard solution of silver nitrate. The concentration of $^{36}Cl^-$ was determined by radioactive counting as described below.

(3) *Mixtures of* I^- *and* Cl^-. The total concentration of halide was determined as before, and the concentration of I^- by a differential conductometric titration with silver nitrate, in an excess of ammonia. Calculations show that the precipitation of silver iodide is complete in the presence of ammonia, and that there is no precipitation of silver chloride when the concentration of ammonia is about 5 to 10 times the concentration of chloride. The method was

tested by titrating a known amount of sodium iodide in ammonia solution, and a mixture of the Cl^- and I^- under the same conditions. The error was $<5\%$.

(4) *Concentration of* $^{36}Cl^-$ *by radioactive counting.* A liquid scintillator was added to part of the remaining concentrated wash solution and the radioactivity counted. Two scintillator solutions were used: the first was prepared from 1,4-di-(5-phenyl-2-oxazolyl)benzene (0·01%) and 2,5-diphenyloxazole (1%) in purified dioxan; and the second from 2,5-diphenyloxazole (1%) in a 3 : 1 propan-1-ol : xylene mixture. These scintillator solutions were selected as they gave good efficiency of counting plus maximum solubility of alkali-metal halide. The solutions were counted either with an Ekco unit (type N530F with liquid scintillation head), or with an Isotopic Developments Ltd., coincidence counter (scaler type 1700, control unit 2032, measuring head 2022).

A portion of the concentrated solution (0·3 c.c.) was weighed into the scintillator solution (3 c.c.) in the counting vial. The small variations in the amount of water introduced, and consequent variations in the quenching effect, were corrected for by applying a factor obtained from calibrations of a standard radioactive solution with different amounts of added water. Since the amount of water introduced in an analysis never varied from the standard by more than a few per cent., the correction was always less than 1·5%. The count rates were reduced by the presence of I^-, and a further correction factor was obtained by plotting the count-rate for a given solution against amounts of added potassium iodide and chloride. The efficiency of the counting was frequently checked against a standard solution of $^{36}Cl^-$. With the Ekco counter, the efficiency could vary by as much as several per cent. per day, in which case the standard was counted before and after a sample. The mean of several different measurements was obtained and referred to the normal value of the standard. This correction was sometimes as high as 4%. The amount of water in the standard sample was the same as in the analyses, and the correction for quenching by the water in this was also applied. An average of 40,000 counts was taken, yielding a statistical error of *ca.* ½%. The background count, which was taken in the same vial as were the analyses, and under the same conditions, varied by less than 5%. Small amounts of sodium or potassium chloride had no detectable effect on the counting efficiencies.

Materials.—Ethyl chloride labelled with chlorine-36. Two samples were made, as described by de la Mare,[3] by means of the exchange reaction between $Li^{36}Cl$ and ethyl chloride. The first yielded ethyl chloride (6 c.c.) with an activity of 4·6 counts/sec./mole, but containing 6% of methyl chloride, presumably from the exchange reaction between $Li^{36}Cl$ and the methanol solvent. To ensure that the ethyl chloride contained a constant proportion of impurity, the sample used for runs was stored as a vapour in a 2 l. bulb. The treatment of results obtained from ethyl chloride containing this impurity is considered below. The second preparation was carried out in ethanol solvent, and the product contained no methyl chloride.

Methyl chloride. Gas from a cylinder (I.C.I.) was passed through a solution of potassium hydroxide, condensed in liquid air, and distilled at carbon dioxide–acetone temperature from phosphorus pentoxide. This was followed by bulb-to-bulb distillation with retention of the middle fraction; this showed no impurities (gas chromatography).

Methyl bromide and iodide. B.D.H. products were thoroughly degassed and bulb-to-bulb distilled with rejection of large head and tail fractions. Methyl iodide was stored in a dark container at liquid-air temperature, and showed no discolouration during use.

Acetyl chloride labelled with chlorine-36. Acetyl chloride was twice distilled from dimethylamine, and the product shaken with $Li^{36}Cl$ at room temperature for 4 days. Labelled acetyl chloride was distilled from the suspension, and the fraction boiling between 51 and 52° collected. Acetyl chloride (6 c.c.), with an activity of 10 counts/sec./mole of potassium chloride product, was obtained.

RESULTS AND DISCUSSION

Reactions of Sodium Atoms with Methyl and Ethyl Chlorides.—The results are given in Table 1, where the rate constants refer to the reactions:

$$\mathrm{Na + MeCl = NaCl + Me} \qquad (1)$$

$$\mathrm{Na + EtCl = NaCl + Et} \qquad (2)$$

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[3] de la Mare, *J.*, 1955, 3169.

In these runs the labelled ethyl chloride contained 6% methyl chloride, and a correction factor (f) had to be applied. The impure ethyl chloride was caused to react alone with sodium over a wide range of temperature, and no variation in the concentration of activity of the sodium chloride product was observed. Hence it was deduced that the specific activities of the ethyl chloride and the methyl chloride impurity were the same. It follows that the concentration of radioactive sodium chloride [$Na^{36}Cl$], from ethyl chloride, is given by [$Na^{36}Cl$(total)] × $\{1 - (0{\cdot}06/K)\}$, where $K = k_2/k_1$, and that $[Et^{36}Cl]_c = [Et^{36}Cl](1 - 0{\cdot}06)$, where $[Et^{36}Cl]_c$ is the actual concentration of ethyl chloride and [$Et^{36}Cl$] is the concentration measured. This gives

$$K = k_2/k_1 = \frac{[Na^{36}Cl(total)]}{[NaCl]} \times \frac{[MeCl]}{[Et^{36}Cl]} \times \frac{\{1 - (0{\cdot}06/K)\}}{1 - 0{\cdot}06} = k^1 f,$$

where the experimental rate constant,

$$k^1 = \frac{[Na^{36}Cl(total][MeCl]}{[NaCl][Et^{36}Cl]},$$

and the correction factor,

$$f = \{1 - (0{\cdot}06/K)\}/(1 - 0{\cdot}06). \qquad \text{(A)}$$

Since the values of f were small, they could be calculated from k^1 instead of K. Log k^1 was plotted against $1/T$, and f calculated at each temperature by replacing K in equation (A) by the value obtained from the straight-line graph. It is to be seen from Table 1 that the correction introduced by f is *ca.* 1%. The reproducibility of the analysis was checked by analysing two fractions in some runs. The errors in titration and counting are both estimated at *ca.* ±1%, and since the concentration of sodium chloride from methyl chloride is calculated by difference, the total error should be < ±4%. No larger errors were observed in the duplicate analyses and hence systematic errors did not occur.

TABLE 1.

Reactions of sodium atoms with methyl and ethyl chlorides.

Run	Temp.	N_2 pressure (mm. Hg)	Flow rate (c.c. sec.$^{-1}$)	Na input (μ mole hr.$^{-1}$)	$\frac{MeCl}{EtCl}$	$\frac{(MeCl + EtCl)}{Na}$	Product analysed (μ mole)	f	k_2/k_1
53	292°	9	34	10	1·592	250	8	1·015	1·331
62	292	9·5	38	15	1·886	100	17	1·015	1·306
61	300	10·5	35	13	1·886	120	12	1·015	1·313
68*a*	303	9·5	38	38	1·134	82	25	1·015	1·312
68*b*	303	9·5	38	38	1·134	82	10	1·015	1·342
57	307	9	35	26	1·592	92	22	1·015	1·353
63*a*	323	9·5	38	34	1·886	55	15	1·014	1·270
63*b*	323	9·5	38	34	1·886	55	17	1·014	1·309
70*a*	323	10·5	40	43	1·134	80	14	1·014	1·308
70*b*	323	10·5	40	43	1·134	80	14	1·014	1·314
51	326	9	36	30	1·592	75	20	1·014	1·272
56	328	10	36	32	1·592	80	22	1·014	1·268
52	341	11	37	31	1·592	63	42	1·013	1·219
67*a*	343	10	41	49	1·134	55	23	1·013	1·264
67*b*	343	10	41	49	1·134	55	13	1·013	1·240
71*a*	344	9·5	41	42	1·134	100	20	1·013	1·308
71*b*	344	9·5	41	42	1·134	100	15	1·013	1·278
54	348	13·5	29	14	1·592	200	12	1·012	1·267
55	350	11·5	35	32	1·592	60	27	1·012	1·248
64	358	13	31	37	1·134	70	22	1·012	1·251
59*a*	367	11	38	46	1·886	45	22	1·012	1·216
59*b*	367	11	38	46	1·886	45	17	1·012	1·260
60	370	9	38	31	1·886	95	23	1·012	1·249
65	373	11·5	38	45	1·134	55	33	1·012	1·229
69*a*	389	10·5	44	22	1·134	120	20	1·011	1·256
66	391	10·5	42	33	1·134	81	22	1·011	1·247

From Table 1 it is clear that the results were not affected by the amount of product analysed, the ratio of halides, and the ratio of halide to sodium. Furthermore, the results showed no variation when the same mixture of reactants was used for several runs, hence there was adequate mixing of the halides and no selective effusion through the needle-valve. Back-diffusion of reactants is ruled out since the results were independent of changes in the pressure of carrier gas. The possibility of heterogenous exchange reactions of the type

$$R^{36}Cl + NaCl = RCl + Na^{36}Cl$$

has to be carefully considered. If a portion of the $Na^{36}Cl$ had been formed in this way, then the results would have been dependent upon the pressure of alkyl halide. Perhaps the best evidence in favour of the $Na^{36}Cl$ arising from a homogeneous reaction, and not from heterogeneous exchange, is the excellent agreement between the present results and those from the diffusion-flame technique, where heterogeneous reactions do not occur. The detailed comparison of results is presented later. Lengthy discussion of the possible formation of significant amounts of sodium chloride from secondary reactions is unnecessary since the results were consistent over a wide range of experimental conditions. It is safe to assume, then, that the sodium chloride was formed in reactions (1) and (2), and at least-mean-squares treatment of the results yields

$$E_1 - E_2 = 608 \pm 83 \text{ cal. mole}^{-1} \text{ and } A_2/A_1 = 0{\cdot}773 \pm 0{\cdot}060.$$

Reactions of Potassium Atoms with Methyl and Ethyl Chlorides.—The results are listed in Table 2. The larger scatter of results compared to the analogous sodium reactions arises from the more difficult analysis. This is shown by the duplicate analyses of run 124, which differ by *ca.* 7%. The reactions concerned are

TABLE 2.

Reactions of potassium atoms with methyl and ethyl chlorides.

Run	Temp.	N_2 pressure (mm. Hg)	Flow rate (c.c. sec.$^{-1}$)	K input (μ mole hr.$^{-1}$)	$\frac{MeCl}{EtCl}$	$\frac{(MeCl + EtCl)}{Na}$	Product analysed (μ mole)	k_4/k_3
118	217°	8	37	15	1·14	150	19	1·204
126	227	10	31	13	1·156	206	20	1·283
119	230	11	37	3	1·156	630	3	1·250
123	235	9	37	22	1·156	120	22	1·175
109	247	10	37	14	1·216	150	14	1·196
124*a*	248	7·5	35	41	1·156	54	32	1·187
124*b*	248	7·5	35	41	1·156	54	13	1·296
114	250	10	37	7	1·14	190	9·5	1·257
125	262	11	31	22	1·156	130	20	1·150
105	287	9·5	37	22	1·216	120	24	1·174
115	294	12	27	5·5	1·14	480	8·2	1·207
106	297	9	37	22	1·216	62	27	1·133
113	303	10	37	10	1·14	300	12	1·128
108	311	10	37	24	1·216	61	28	1·196
110	313	11	37	9	1·216	200	21	1·171
121	315	9	37	12	1·156	180	17	1·154
116	333	10	37	9	1·14	240	13	1·173
117	333	13	31	6	1·14	350	10	1·133

$$K + MeCl = KCl + Me \tag{3}$$

$$K + Et^{36}Cl = K^{36}Cl + Et \tag{4}$$

and a least-mean-square calculation of the results gives

$$E_3 - E_4 = 400 \pm 90 \text{ cal. mole}^{-1} \text{ and } A_4/A_3 = 0{\cdot}83 \pm 0{\cdot}10.$$

Reactions of Potassium Atoms with Methyl and Acetyl Chlorides.—Considerable experimental difficulties were found with this system, owing to the high reactivity of acetyl chloride and the enormous difference in reactivity between it and methyl chloride. Since the acetyl chloride was the labelled halide, it was desirable to produce as much potassium chloride from the methyl chloride as possible, since this quantity was calculated by difference. Rough calculations showed that for 20% of the potassium chloride to come from the methyl chloride, a ratio MeCl : Me·COCl of *ca.* 80 was necessary, under which conditions the errors in titration or counting are multiplied by five. Further, if the consumption of acetyl chloride was to be less than 10%, a ratio MeCl : Na of *ca.* 800 was required. This introduces the problem of back-diffusion of reactants, and reduces the size of the reaction zone. These deductions were confirmed experimentally when it was found that 80% of the reaction occurred inside the jet of the reactor, the potassium chloride being deposited in the nozzle, causing a reduction in the flow rate of carrier gas as the run proceeded. Since it was obviously difficult to obtain sufficiently accurate results for the calculation of relative Arrhenius parameters, it was decided to test the reproducibility of the system at a single temperature. The results at 285 ± 2° are given in Table 3, where the rate constants refer to the reactions

$$\mathrm{K + MeCl = KCl + Me} \qquad (3)$$

$$\mathrm{K + Me{\cdot}COCl = KCl + Me{\cdot}CO} \qquad (5)$$

The mean value of k_5/k_3 is 360. To correct for the consumption of reactants, the ratio MeCl : Me·COCl was calculated from the expression:

$$\frac{[\mathrm{MeCl} - \tfrac{1}{2}\{[\mathrm{KCl}] \text{ from } \mathrm{MeCl}\}}{[\mathrm{Me{\cdot}COCl}] - \tfrac{1}{2}\{[\mathrm{KCl}] \text{ from } \mathrm{Me{\cdot}COCl}\}}.$$

This is only an approximate correction but the error it introduces is smaller than the experimental error.

The ratios (k_5/k_3) in Table 3 were obtained by analysing the potassium chloride obtained in the collection cylinder, but with run 160 the solid deposited in the nozzle of the reactor was also analysed. The much lower ratio obtained ($k_5/k_3 = 75$) could be due to wall reactions or to depletion of the acetyl chloride inside the jet. With acetyl chloride as one of the reactants, a very small amount of involatile organic material was always deposited in the cylinder. The possibility that this material contained the ‑COCl group, which on hydrolysis would yield hydrochloric acid, was ruled out by the fact that the results were independent of percentage conversion and composition of the reactant mixture. The further possibility, that this organic material might introduce additional radioactivity into the wash water, was tested in the following way. In one analysis the wash solution was divided into two fractions, one of which was analysed in the usual way and the other evaporated to dryness and the organic content eliminated before the salt was redissolved and the second analysis performed. There was excellent agreement between the analyses, so that this rules out interference of the small organic residue with the radioactive counting. Another feature of the runs involving very reactive halides concerns the distribution of the solid product in the collection cylinder of the reactor. Two deposit zones were formed:

TABLE 3.

Reactions of potassium atoms with methyl and acetyl chlorides at 285°.

Run	N_2 or He pressure (mm. Hg) *	Flow rate (c.c. sec.$^{-1}$)	$\frac{\mathrm{MeCl}}{\mathrm{AcCl}}$	Percentage conversion †	k_5/k_3
160	8	36	123	1·2	261
144	10	20	183	0·5	434
140	11	21	99	7	336
143	12	25	81	2·7	396
141	13	25	183	2·1	392

* For run 160, carrier gas was N_2 (for other runs, He). † Percentage conversion based on consumption of AcCl and KCl collected in the cylinder, not in the jet.

one, 3 or 4 cm. wide, homogeneously around the jet; and the other at the beginning of the cold part of the cylinder. The latter appeared as a white spot with clearly defined edges. It was possible to analyse these deposits separately in two runs, one with acetyl chloride–methyl iodide and the other with acetyl chloride–methyl bromide. It was found that the deposit around the jet was richer in Cl^- than the deposit on the cold part of the cylinder, and that the effect was greater in the run with methyl iodide. There is no obvious explanation of these findings.

Reactions of Potassium Atoms with Methyl Iodide and Ethyl Chloride.—Two runs, presented in Table 4, were carried out at 285°, to check the internal consistency of the overall results. The expected high experimental error is confirmed by the duplicate analyses of run 166. The reactions concerned are

TABLE 4.

Reactions of potassium atoms with methyl iodide and ethyl chloride at 285°.

Run	N_2 pressure (mm. Hg)	Flow rate (c.c. sec.$^{-1}$)	$\frac{EtCl}{MeI}$	K input (μ mole hr.$^{-1}$)	Product analysed (μ mole)	Percentage conversion *	k_6/k_4
166*a*	6	18	23	5·6	4·95	1·6	32
166*b*	6	18	23	5·6	3·1	1·6	34
167	8	15	23	3·5	4·7	1·6	43

* Percentage conversion based on consumption of CH_3I.

$$K + MeI = KI + Me \qquad (6)$$

$$K + EtCl = KCl + Et \qquad (4)$$

and the mean value of $k_6/k_4 = 38$.

Reactions of Sodium and Potassium Atoms with Methyl Iodide and Acetyl Chloride.—The analytical conditions were such that the reactions could be studied over a range of temperatures and a variety of other experimental conditions. The results with potassium are given in Table 5 where the rate constants are defined by the reactions

$$K + MeCOCl = KCl + MeCO \qquad (5)$$

$$K + MeI = KI + Me \qquad (6)$$

Most of the potassium chloride was found in the jet of the reactor, and analysis of this product showed that the reactions inside the jet were less selective than those which gave a deposit on the cylinder. That there was no transport of potassium chloride from the jet to cylinder was shown by the fact that the results were independent of whether or not the jet was cleared before the run was started. The results of two runs in which sodium replaced

TABLE 5.

Reactions of potassium atoms with methyl iodide and acetyl chloride at 285°.

Run	Temp.	N_2 pressure (mm. Hg)	Flow rate (c.c. sec.$^{-1}$)	$\frac{MeI}{AcCl}$	Percentage conversion *	k_5/k_6
158	238°	6	36	2·64	0·71	6·85
150	241	8	48	2·53	1·0	7·02
146	255	8	36	1·0	0·4	7·05
147	278	9	32	1·0	0·1	7·20
157	279	10	34	2·64	0·78	7·32
148	289	5	32	1·0	0·6	6·87
153	298	6	36	2·53	2·2	6·18
164 †	300	7	36	2·32	0·2	6·80
165 †	300	9	34	2·32	0·2	7·56
159	313	5	36	2·53	0·9	6·65
151	315	10	48	2·53	10·0	3·40
152	322	11	54	2·53	0·84	7·71

* Based on consumption of AcCl, and KCl collected in cylinder. † Sodium used instead of potassium.

potassium are also shown in Table 5; both sets of values have been corrected for consumption of reactants by use of the approximate expression previously discussed. When the ratio of linear velocity of carrier gas in the nozzle to diffusion coefficient of potassium atoms in the carrier gas was changed by a factor of twenty, the results showed no trend. A dependence of k_5/k_6 on percentage conversion is revealed by runs 151 and 153, but, provided the conversion is kept low, the results are independent of experimental conditions. Disregarding runs 151 and 153, the results derived from the best straight line through the points on the Arrhenius plot are

$$E_6 - E_5 = 0 \text{ and } A_5/A_6 = 7{\cdot}0.$$

There is insufficient data to warrant a statistical treatment. The agreement between the ratios from the experiments with sodium and those from the experiments with potassium indicates that the analogous reactions with sodium also have low or zero activation energies.

Reactions of Potassium Atoms with Methyl Bromide and Acetyl Chloride.—The reactions concerned are

$$\mathrm{K + MeBr = KBr + Me} \qquad (7)$$

$$\mathrm{K + MeCOCl = KCl + MeCO} \qquad (5)$$

The results are shown in Table 6. From the Arrhenius plot

$$E_7 - E_5 = 1{\cdot}4 \text{ kcal. mole}^{-1} \text{ and } A_5/A_7 = 3{\cdot}5.$$

Reactions of Potassium Atoms with Methyl Bromide and Ethyl Chloride.—The results and experimental conditions are shown in Table 7. The reactions are

$$\mathrm{K + MeBr = KBr + Me} \qquad (7)$$

$$\mathrm{K + EtCl = KCl + Et} \qquad (4)$$

and from the Arrhenius plot

$$E_4 - E_7 = 4{\cdot}4 \text{ kcal. mole}^{-1} \text{ and } A_7/A_4 = 0{\cdot}52.$$

TABLE 6.

Reactions of potassium atoms with methyl bromide and acetyl chloride.

Run	Temp.	N_2 pressure (mm. Hg)	Flow rate (c.c. sec.$^{-1}$)	Rate of formation of KCl (μ mole hr.$^{-1}$)	$\frac{\mathrm{MeBr}}{\mathrm{AcCl}}$	Percentage conversion *	k_7/k_5
170	229°	7	36	9·5	27·5	2·1	15·0
170	229	7	36	9·5	27·5	2·1	14·9
179	239	5	36	7·5	32·6	1·8	13·6
179	239	5	36	7·5	32·6	1·8	13·9
169	286	7	36	3·2	27·9	0·5	12·6
171	309	5	36	4·6	27·5	0·8	11·7
180	318	7	32	2·8	32·6	0·4	11·7

* Based on consumption of AcCl, and KCl collected in cylinder.

TABLE 7.

Reactions of potassium atoms with methyl bromide and ethyl chloride.

Run	Temp.	N_2 pressure (mm. Hg)	Flow rate (c.c. sec.$^{-1}$)	K input (μ mole hr.$^{-1}$)	$\frac{\mathrm{EtCl}}{\mathrm{MeBr}}$	$\frac{\mathrm{MeBr + EtCl}}{\mathrm{Na}}$	k_7/k_4
185	230°	7	36	4·8	6·75	340	48·9
186	262	8	36	7·1	6·75	400	32·9
183	287	7	36	8·35	6·75	500	26·5
183	287	7	36	8·35	6·75	500	29·6
187	312	6	36	8·4	6·75	370	26·3
184	316	6	36	19·0	6·75	200	25·4
184	316	6	36	19·0	6·75	200	25·8

Comparison of Results.—The internal consistency of the results presented here can be checked by calculating indirectly the ratio of rate constants (k_5/k_3) for the reactions of potassium atoms with acetyl chloride and methyl chloride at 285° and comparing the values with the experimental value. k_5/k_3 can be calculated in two ways:

$$k_5/k_6 \times k_6/k_4 \times k_4/k_3 = k_5/k_3 = 320;$$

and

$$k_5/k_7 \times k_7/k_4 \times k_4/k_3 = k_5/k_3 = 430.$$

When compared with the experimental value of 360, the agreement is within the experimental errors, which are fairly large owing to the difficult analyses in some of the determinations.

The results of Hartel, Meer, and Polanyi [4] are directly comparable with those of the present study. They investigated the reactions of sodium atoms with methyl and ethyl chlorides, concentrating on relative rate constants under similar experimental conditions, and at 275° found $k_2/k_1 = 1{\cdot}41$ which corresponds well with the value (1·35) obtained from our Arrhenius plot.

Comparison of Reactivities of Sodium and Potassium Atoms.—Several workers have reported absolute rate constants for the reactions of sodium atoms with methyl chloride, bromide, and iodide and with acetyl chloride. The results are generally consistent within an order of magnitude but differences of a factor of five or six are commonly found. The best way of obtaining relative rate constants is to compare results obtained by the same method and experimental conditions, the same boundary conditions, and use of the same transition-state model. This is impossible when the reactants have large differences in reactivity, so one must compromise and obtain results from the same workers. Table 8 has been drawn up along these lines and leads to the first column of relative rate constants in Table 9 (Table 9 also includes our results with potassium). The relative rate constants for sodium reactions obtained in this rather unsatisfactory way from the literature are probably only accurate to an order of magnitude, but nevertheless they form a useful basis for comparison.

TABLE 8.

Reactions of sodium atoms with methyl halides and acetyl chloride.

Reactant	Temp.	Method	$10^{-11} k$ (mole^{-1} c.c. sec.$^{-1}$)	Reactant	Temp.	Method	$10^{-11} k$ (mole^{-1} c.c. sec.$^{-1}$)
MeCl	323°	Modified flame [5]	66	MeI	240	Diffusion flame [9]	3100
	313	Diffusion flame [6]	12·6		250	Diffusion flame [10]	445
	267	Diffusion flame [7]	9		255	Mean life [10]	486
	257	Diffusion flame [8]	10		277	Diffusion flame [11]	410
	220	Mean life [9]	6				
				Me·COCl	270	Diffusion flame [8]	1000
MeBr	240	Diffusion flame [8]	200		247	Diffusion flame [12]	250
	200	Mean life [9]	15				
	220	Mean life [9]	17·2				
	242	Mean life [9]	60				

Relative rate constants for sodium reactions may be calculated from those for potassium by the semi-empirical method of Eyring and Polanyi [1] together with later modifications of Evans and Polanyi.[13] By considering potential-energy curves for reactions of the general type

$$M + RX = MX + R$$

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[4] Hartel, Meer, and Polanyi, *Z. phys. Chem.*, 1932, *B*19, 139.

[5] Reed and Rabinowitch, *J. Chem. Phys.*, 1957, **27**, 988.

[6] Reed and Rabinowitch, *J. Phys. Chem.*, 1957, **61**, 598.

[7] Heller and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 633.

[8] Hartell and Polanyi, *Z. phys. Chem.*, 1930, *B*11, 97.

[9] Frommer and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519.

[10] Haresnape, Stevels, and Warhurst, *Trans. Faraday Soc.*, 1940, **36**, 465.

[11] Whittle, Ph.D. thesis, Manchester, 1951.

[12] Trotman-Dickenson, "Gas Kinetics," Butterworth, London, 1955, p. 219.

[13] Evans and Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11.

TABLE 9.

Relative rate constants for reactions of sodium and potassium atoms at 285°.

Reactant (1)	Reactant (2)	k_1/k_2		
		Na (lit.)	Na (calc.)	K (this work)
MeCOCl	MeCl	500	<2400	400
MeCOCl	MeBr	5	<75·6	12·6
MeCOCl	MeI	0·5	7·0	7·0
MeBr	MeCl	100	>34·5	34·5
MeI	MeCl	1000	<342	57
MeI	MeBr	10	<11	1·8

where M = alkali metal and RX = alkyl halide, it has been shown that there is a relation between the difference in activation energies (ΔE) and the difference in enthalpy changes $\{\Delta(\Delta\mathrm{H})\}$ for pairs of these reactions, as follows:

$$\Delta E = -\alpha\Delta(\Delta\mathrm{H}) \qquad \text{(B)}$$

where $0 < \alpha < 1$. Butler and Polanyi[14] studied the reactions of sodium atoms with a series of alkyl chlorides and obtained a value of $\alpha = 0{\cdot}28$, but this result now seems doubtful.[15]

To apply this treatment to the present results, it is necessary to assume that the reactions of sodium and potassium atoms with acetyl chloride and methyl iodide have zero activation energy. The measurements of Herschbach and his co-workers,[16] using molecular-beam techniques on the potassium–methyl iodide system indicate that this reaction has an activation energy of <0·3 kcal. mole^{-1}. Evidence for this basic assumption was also obtained in the present work when it was shown (see Table 5) that the same ratio of rate constants for these reactants was obtained when potassium was replaced by sodium. Furthermore, since it is probable that the shapes of the energy surfaces and the resonance energies in the activated state will be different for acetyl chloride and methyl iodide reacting with either sodium or potassium atoms, it seems unlikely that the same rate constants would have been obtained if the reactions involved appreciable activation energies. It is also necessary to assume, in this treatment, that the relative *A*-factors are constant when sodium replaces potassium. This does not introduce a significant error.

Thus, calculations based on the semi-empirical method of Evans and Polanyi,[13] and the assumptions stated above, lead to the relation:

$$E_{(\mathrm{Na+MeBr})} - E_{(\mathrm{K+MeBr})} < E_{(\mathrm{Na+MeCl})} - E_{(\mathrm{K+MeCl})} < 2\ \text{kcal. mole}^{-1}.$$

Hence the second column of relative rate constants in Table 9 has been obtained. Two serious discrepancies are revealed between the sodium results obtained from the literature and those calculated from our potassium results. First, the reactivity of acetyl chloride is found to be much higher in the present study, and secondly, the value for the ratio of rate constants for methyl iodide and chloride is much lower.

Absolute Activation Energies.—By making the assumption, previously discussed, that the reactions of sodium and potassium atoms with acetyl chloride have zero activation energy, absolute *E* values can be obtained from the present study, as listed below:

Reactant	*E* (kcal.mole^{-1})		Reactant	*E* (kcal.mole^{-1})	
	K	Na		K	Na
MeI	0	0	MeCl	6·2	8·2
MeBr	1·4	3·4	EtCl...........................	5·8	7·8

The values for sodium reactions are only approximate. There have been no previous determinations of Arrhenius parameters for the reactions of potassium atoms. The

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[14] Butler and Polanyi, *Trans. Faraday Soc.*, 1943, **39**, 19.

[15] Ref. 12, p. 230.

[16] Herschbach, Kwei, and Norris, *J. Chem. Phys.*, 1961, **34**, 1842.

activation energy for the reaction of sodium atoms with methyl bromide compares reasonably well with the value of *ca.* 5 kcal. mole^{-1} obtained [10] from the rate constant at a single temperature, while that for the sodium–methyl chloride reaction is in good agreement with the value of 7·5 kcal. mole^{-1} obtained by Hartel and Polanyi.[8] The work of Cvetanovic and Le Roy [17] on the reaction of sodium atoms with ethyl chloride is the only instance where emphasis has previously been placed on measuring the temperature coefficient of the reaction. By assuming that the diffusion coefficient (D) of sodium vapour in nitrogen varies with temperature such that $(D/T)^{3/2}$ is constant for a given pressure of nitrogen, they obtained $E = 10{\cdot}0 \pm 0{\cdot}5$ kcal. mole^{-1}, as compared with *ca.* 7·8 kcal. mole^{-1} found here. Cvetanovic and Le Roy's result agrees well with the value from a rate constant at a single temperature and the assumptions that the collisional cross-section is $3{\cdot}5 \times 10^{-15}$ cm.^{2} and that the steric factor is unity. The corresponding A-factor is, however, 10^{15} mole^{-1} c.c. sec.$^{-1}$, which seems rather high, and, in conjunction with the general limitations of the method, might throw some doubt on the estimated accuracy of their activation energy.

Relative A-*Factors*.—The experimental relative A-factors for the potassium reactions are given below together with the derived values for the reactions of potassium atoms with methyl chloride and bromide and methyl chloride and iodide:

Reactant (1)	Reactant (2)	A_1/A_2	Reactant (1)	Reactant (2)	A_1/A_2
MeCOCl	MeI	7·0	EtCl	MeCl	0·83
MeCOCl	MeBr	3·5	MeCl	MeBr	2·3
MeBr	EtCl	0·52	MeCl	MeI	4·6

These experimental values can be compared with theoretical values obtainable from transition-state theory, according to the equation:

$$A = (e^2\mathbf{k}T/\mathbf{h}) \exp [\Delta S^{\ddagger}_{\text{(trans.)}} + \Delta S^{\ddagger}_{\text{(rot.)}} + \Delta S^{\ddagger}_{\text{(vib.)}}],$$

in which the symbols have their usual meaning. The method has been applied previously to the calculation of relative A-factors for the competitive reactions of halogen atoms with hydrocarbons,[18] and we have used it here to test the (A_1/A_2) values for the reactions of potassium atoms with MeCl–MeBr and MeCl–MeI. We have estimated the lengths of the C–X bond in the activated complex from the crossing point of the energy surfaces by use of the semi-empirical method. If it is assumed that the three atoms in the complex, C–X–K, are linear, then there is no change in the symmetry factor for any of these reactions. The angles were assumed to be tetrahedral and the following bond distances were employed:

Molecule or Complex	Bond	Distance (Å)	Molecule or Complex	Bond	Distance (Å)
MeCl	C–H	1·11	MeI	C–I	2·14
	C–Cl	1·78	MeIK	C–I	2·38
MeClK	C–Cl	2·16		I–K	3·23
	Cl–K	2·79	EtCl	C–H (pri)	1·02
MeBr	C–Br	1·94		C–H (sec)	1·2
MeBrK	C–Br	2·24		C–C	1·54
	Br–K	2·94		C–Cl	1·78
			EtClK	C–Cl	2·16
				Cl–K	2·79

It was also assumed that the angles and bond distances remained constant other than for the bond being broken. The values of the entropy changes, calculated in the usual way, are listed below:

Reactant	$\Delta S^{\ddagger}_{\text{trans.}}$ (cal. deg.$^{-1}$)	$\Delta S^{\ddagger}_{\text{rot.}}$ (cal. deg.$^{-1}$)	Reactant	$\Delta S^{\ddagger}_{\text{trans.}}$ (cal. deg.$^{-1}$)	$\Delta S^{\ddagger}_{\text{rot.}}$ (cal. deg.$^{-1}$)
MeCl	−17·5	4·32	MeI	−18·3	3·86
MeBr	−18·0	3·94	EtCl	−17·6	3·7

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[17] Cvetanovic and Le Roy, *J. Chem. Phys.*, 1952, **20**, 1016.
[18] Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937.

The values for ethyl chloride, also listed above, are referred to later. The contribution from vibrational entropy is more difficult to evaluate. To a first approximation, the loss of the C–X stretching vibration in the initial molecule is compensated by the asymmetrical stretching vibration of C–X–K in the activated complex. It may be further argued that the contributions of the two bending vibrations in different reactants will be about equal, bearing in mind that the heaviest molecule is the least stretched when the activated state is reached. Relative *A*-factors are thus obtained from the expression

$$A_1/A_2 = \exp\,[\Delta S^{\ddagger}_{1(\mathrm{trans})} + \Delta S^{\ddagger}_{1(\mathrm{rot.})}]/\exp\,[\Delta S^{\ddagger}_{2(\mathrm{transl.})} + S^{\ddagger}_{2(\mathrm{rot.})}].$$

From this simplified picture the calculated values are $A_{\mathrm{MeCl}}/A_{\mathrm{MeBr}} = 1{\cdot}6$ and $A_{\mathrm{MeCl}}/A_{\mathrm{MeI}} = 1{\cdot}9$. The experimental values are 2·3 and 4·6. The agreement is not very good, possibly owing to the omission of the vibrational entropy term.

Absolute A-*factors*.—From the absolute activation energies and absolute rate constants, calculated from the experimental relative rate constants on the basis of an *A*-factor corresponding to the collision number for the reaction of potassium atoms with methyl iodide, absolute values of the *A*-factors for the reactions being considered are readily obtained. For instance, for the reaction of sodium atoms with methyl bromide, the *A*-factor is $1{\cdot}8 \times 10^{14}$ mole^{-1} c.c. sec.$^{-1}$. This is in keeping with other metathetical reactions in which the attacking entity is an atom. Such a value is, however, too high in comparison with the calculated *A*-factor of about 10^{11} mole^{-1} c.c. sec.$^{-1}$, based on a rigid activated complex and changes only in rotational and translational entropies. The most plausible explanation of this discrepancy is that the activated complex may be non-linear in CXK, because of additional rotational entropy of the complex.

Comparison of the Reactions of Methyl and Ethyl Chlorides.—Our results have shown that the differences in reactivity between methyl and ethyl chloride towards sodium or potassium atoms are due to lower activation energies for the ethyl chloride reactions and not, as previously thought,[19] due to differences in the *A*-factors.

These ΔE values cannot quantitatively be accounted for by the semi-empirical theory of activation energies. The experimental ratio of *A*-factors ($A_{\mathrm{EtCl}}/A_{\mathrm{MeCl}} = 0{\cdot}83$), on the other hand, compares well with the value calculated from transition-state theory, 0·69—0·81.

Reactions of Alkyl Radicals Generated in Flame Reactions.—An attempt was made to study the reactions of ethyl radicals produced by the reactions of ethyl chloride with sodium and potassium atoms. The hydrocarbon products, analysed by gas chromatography, consisted mainly of ethane, ethylene, and *n*-butane, but also contained small amounts of propane (*ca.* 3%, with respect to *n*-butane). From fourteen experiments, the following average ratios were obtained:

$$R_{\mathrm{C_2H_6}}/R_{\mathrm{C_2H_4}} = 1{\cdot}1 \pm 0{\cdot}2,\quad R_{\mathrm{C_2H_6}}/R_{\mathrm{C_4H_{10}}} = 0{\cdot}44 \pm 0{\cdot}06,$$

and $R_{\mathrm{C_2H_4}}/R_{\mathrm{C_4H_{10}}} = 0{\cdot}39 \pm 0{\cdot}06$, where R_x = rate of formation of X.

Rough calculations showed that, under the conditions of the experiments, little hydrogen abstraction by ethyl radicals should have occurred from the parent alkyl halide. Ideally then, the ratio of ethane or ethylene to n-butane should equal the disproportionation : combination ratio of rate constants for ethyl radicals, *i.e.*, from

$$2C_2H_5 = C_2H_6 + C_2H_4 \qquad (8)$$

$$2C_2H_5 = n\text{-}C_4H_{10} \qquad (9)$$

$k_8/k_9 = \Delta(\mathrm{Et,Et}) = R_{\mathrm{C_2H_4}}/R_{\mathrm{C_4H_{10}}} = R_{\mathrm{C_2H_6}}/R_{\mathrm{C_4H_{10}}}$. The reactions of ethyl radicals are well established and Δ(Et,Et) is known to be 0·12—0·13 independent of the source of radicals, provided the radicals are thermally equilibrated. In the present alkali-metal flame system, there would appear to be enhanced rates of formation of ethane and ethylene. Possible sources of these increased rates are (1) secondary reactions involving sodium or

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[19] Smith and Eyring, *J. Amer. Chem. Soc.*, 1952, **74**, 229.

potassium atoms, (2) heterogeneous reactions in the fog of alkali-metal salt, and (3) " hot " radical reactions. From our experiments it is impossible to decide which, if any, of the possible reactions is responsible for the anomalous results.

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