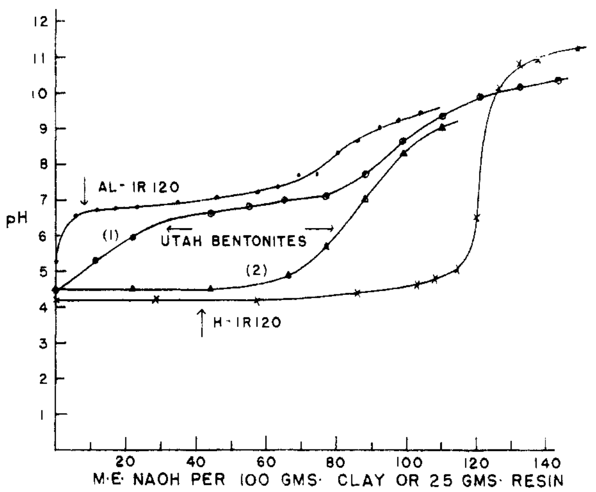

Fig. 1.—Potentiometric titration curves of H- and Al-Amberlite IR-120 and of acid Utah bentonites prepared by (1) leaching with 0.1 N HCl and (2) leaching with 1 *N* HCl.

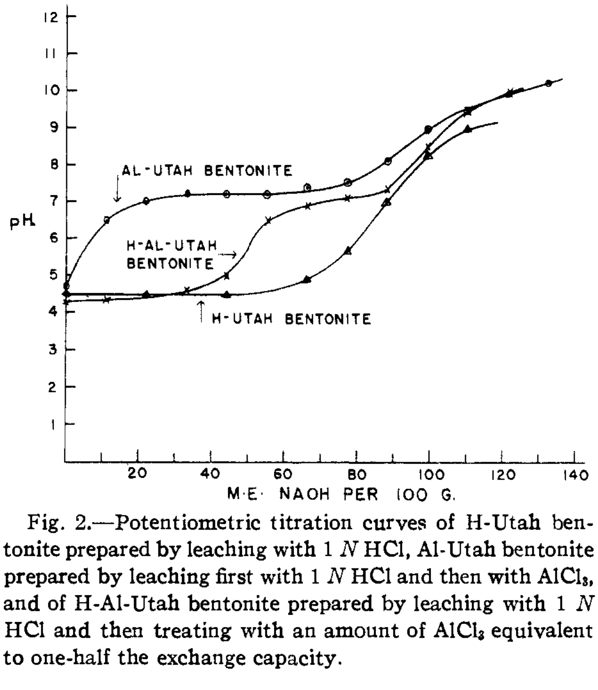

Fig. 2.—Potentiometric titration curves of H-Utah bentonite prepared by leaching with 1 *N* HCl, Al-Utah bentonite prepared by leaching first with 1 *N* HCl and then with $AlCl_3$, and of H-Al-Utah bentonite prepared by leaching with 1 *N* HCl and then treating with an amount of $AlCl_3$ equivalent to one-half the exchange capacity.

the $AlCl_3$-leached clay, as well as of the 0.05 *N* HCl-leached and of electrodialyzed clay, varied between −5.4 and −6.4 kcal. per mole of NaOH consumed.

TABLE I

HEATS OF NEUTRALIZATION (KCAL. PER EQUIVALENT) OF ACID CLAYS AND EXCHANGE RESINS

	Method of preparation				
Material	Electro-dialyzed	Leached with 0.05 *N* HCl	Leached with 1 *N* HCl	Col-umned	Leached with $AlCl_3$
Wyoming bentonite	−5.8	...	....	−13.4	
Utah bentonite	−6.4	−6.2	−13.5	−13.5	−5.4
IR-120	...	...	−13.6	....	−5.7

Exchangeable Al and exchangeable H can be replaced from clays and other cation exchangers by exhaustive leaching with neutral salt solutions.[3,4] The clays studied here were leached with *N* KCl and H and Al were determined in the leachate. For electrodialyzed bentonite, 0.05 or 0.1 *N* HCl-leached bentonite, and $AlCl_3$-leached bentonite, 95–100% of the titratable acidity in the KCl leachate was Al. For *N* HCl-leached bentonite and for columned bentonite, 90–100% of the titratable acidity was H. On storage of the latter two clays, a gradual increase in exchangeable Al and decrease in exchangeable H was observed.

The authors conclude from this that Slabaugh worked with H-Al clays, rather than with clays containing exchangeable H in different energy states.

DEPARTMENT OF AGRONOMY
N. C. STATE COLLEGE
RALEIGH, NORTH CAROLINA

The Reactivity of Primary Alkyl Halides with Sodium Thiocyanate

BY THOMAS I. CROWELL

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Many examples of the reactivity of the straight-chain alkyl halides in displacement reactions indicate a minimum in rate for the *n*-butyl derivative; further lengthening of the molecule increases the reaction rate.[1] Although the equilibrium counterpart of this interesting kinetic phenomenon has been investigated by Brown, Taylor and Sujishi,[2] no series of rate constants sufficiently accurate to establish its existence or magnitude can be found.

A convenient reagent for such a comparison is the nucleophilic thiocyanate ion.[3] The reaction of sodium thiocyanate with alkyl bromides, described in this paper, is easily followed at constant ionic

$$RBr + NaSCN \longrightarrow RSCN + NaBr$$

strength and is homogeneous in alcoholic solution owing to the moderate solubility of sodium bromide.

Table I shows one of the runs made with *n*-hexyl bromide. All the results are summarized in Table

TABLE I

SAMPLE DATA FOR *n*-HEXYL BROMIDE[a]

t, min.	KIO_3, ml.	10^5 *k*, l./mole-sec.
0	20.89[b]	..
1355	19.20	1.18
3057	17.49	1.24
4317	16.60	1.22
5688	15.78	1.22
8826	14.39	1.22
11500	13.60	1.21
14184	13.09	1.17

[a] Initially 0.0960 *M*. [b] Corresponds to 0.2002 *M* NaSCN in sample.

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(2) H. C. Brown, M. D. Taylor and S. Sujishi, THIS JOURNAL, **73**, 2464 (1951).

(3) B. Holmberg, *Z. physik. Chem.*, **97**, 134 (1921); V. K. LaMer and J. Greenspan, THIS JOURNAL, **54**, 2739 (1932); A. G. Ogston, *et al.*, *Trans. Faraday Soc.*, **44**, 45 (1948); C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

TABLE II

RATE OF REACTION OF RBr WITH 0.2 *M* NaSCN

R	Purity, %	No. of runs	$10^5 k$, l./mole-sec.
Ethyl	..	3	1.67
n-Propyl	99.5	2	1.15
n-Butyl	99.8	3	1.14
n-Amyl	99.6	3	1.20
n-Hexyl	99.8	2	1.22
n-Heptyl	99.4	2	1.24
n-Octyl	99.0	6	1.27
n-Decyl	98.6	2	1.23
Cetyl	98.3	3	1.20
Isobutyl	99.4	1	0.05
Isoamyl	..	1	0.73
Isohexyl	98.7	2	1.23

II. The average deviation from the mean *k* was less than 1% for each of the alkyl halides except *n*-amyl bromide, for which it was 1.3%, and isobutyl and isoamyl bromides, where only one run was made. There can be no doubt that *n*-amyl bromide is considerably more reactive than *n*-butyl bromide and that the reactivity increases with increasing chain length so that *k* for *n*-octyl bromide is 11% higher than for *n*-butyl bromide. The reactivity of the 10- and 16-carbon bromides appears to be slightly lower, though the lower degree of purity of these compounds causes some uncertainty in the value of *k*.

The data of Table II refer to an initial molarity of alkyl bromide of about 0.09. Because of the considerable differences in molecular weight, however, the percentage by weight of alkyl halide varied from 1.0 to 3.6. That this slight change in the medium was not entirely responsible for the variation in Table II was demonstrated by five experiments in which the molarity of *n*-octyl bromide ranged from 0.05 to 0.14. The extreme values of *k* differed by only 2% and moreover indicated the usual decrease in rate with increasing alkyl bromide concentration.[4]

It is difficult to formulate any simple effect of the alkyl group which would lead to greater reactivity with increasing chain length. An inductive effect should reduce the rate by increasing the electron density at the reaction center. Steric hindrance of the attacking reagent by the longer chain, as proposed by Brown, Taylor and Sujishi,[2] to explain the comparatively low basicity of *n*-propylamine in aqueous solution, would also decrease the rate here. The most satisfactory explanation, however, lies in the fact that the C–Br bond energy gradually decreases from 68.5 to 63.5 kcal./mole as the series is ascended from methyl to butyl bromide,[5] and probably decreases somewhat further in the higher derivatives. Although the small differences in activation energy corresponding to these rate differences would be difficult to measure experimentally, the activation energies of several displacement reactions have been found to decrease slightly when the halide is changed from ethyl to *n*-propyl, though an entropy effect decreases the rate.[4]

Table II also shows that although isobutyl and isoamyl bromides react more slowly than their straight-chain isomers, the branching of the chain in isohexyl bromide is too far from the reaction center to affect the rate.

Experimental

Materials.—Commercially available alkyl bromides were shaken with H_2SO_4, washed with water, dried over K_2CO_3 and fractionated. The purity given in Table II was estimated by Volhard titration for bromide after hydrolysis in a sealed tube. Isohexyl bromide (1-bromo-4-methylpentane) was prepared from formaldehyde and isoamyl alcohol by the Grignard reaction.[6] Eimer and Amend C.P. sodium thiocyanate, dried at 130° for 24 hours, assay (Volhard) 99.8°, was used. The solvent was 95% ethanol (d^4_{25} 0.8004–0.8010).

Procedure.—The kinetic runs were started by weighing the alkyl bromide into a 100-ml. volumetric flask containing 25 ml. of solvent, adding 50 ml. of 0.4 *M* NaSCN (alcoholic) and diluting to the mark at 25.00°. Five-milliliter samples were withdrawn at one- or two-day intervals and added to 30 ml. of water. After adding 7 ml. of 0.5 *M* KCN and 50 ml. of 3 *M* HCl, the sample was titrated for thiocyanate with standard KIO_3 and starch indicator.[7] The Volhard titer of the reaction mixture remained constant, and 99% of the theoretical quantity of thiocyanate ion was consumed after two months. This procedure parallels the standard preparation of alkyl thiocyanates.

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[5] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, pp. 77–79.

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[7] W. C. Oesper, "Newer Methods of Volumetric Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1938, p. 85.

COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA

The Preparation of Acyl Trifluoroacetates from Trifluoroacetic Anhydride

BY WILLIAM D. EMMONS, KEITH S. MCCALLUM AND ARTHUR F. FERRIS

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Recently the preparation of acyl trifluoroacetates from silver trifluoroacetate and acyl halides in ether has been reported.[1] It has now been established that acyl trifluoroacetates may be obtained in good yields from equimolar quantities of trifluoroacetic anhydride and carboxylic acids. Satisfactory procedures have been worked out for the preparation of benzoyl trifluoroacetate (55% yield), lauroyl trifluoroacetate (59% yield), furoyl trifluoroacetate (63% yield) and phenylacetyl trifluoroacetate (53% yield). Thus the hypothesis that the high order of reactivity of trifluoroacetic anhydride–carboxylic acid mixtures in acylation reactions is due to the *in situ* formation of the acyl trifluoroacetate is probably correct.[2]

$$RCOOH + CF_3COOCOCF_3 \longrightarrow RCOOCOCF_3 + CF_3COOH$$

We were originally interested in examination of the equilibrium between trifluoroacetic anhydride and carboxylic acids. The availability of pure samples of acyl trifluoroacetates made possible the development of an infrared procedure for following this reaction. Accordingly, the reaction between benzoic acid and trifluoroacetic anhydride was studied in *n*-butyl ether and in acetonitrile. Each of

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[2] E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).