important pyrolytic products from methyl *n*-butyl ketone, in contrast to the photochemical decomposition at low temperatures there are other products formed in comparable amounts. Moreover, the results from the experiments with added inhibitor show that in the thermal decomposition acetone and propylene are formed mainly by a free radical chain process rather than by a single-step reaction.

A detailed treatment of the kinetics of a free radical mechanism has not been attempted on account of the complexity of the chain decomposition which probably involves the participation of a number of different radicals. The inhibiting effect of propylene indicates that even in the relatively early stages of the decomposition a partial inhibition of the reaction by the products should be taken into account. In the later stages the subsequent reaction of several of the primary products would be expected to introduce additional complicating factors.

Carbonium Ions. V. The Nature of the *t*-Butyl Cation as Indicated by a Study of the Formation of N-*t*-Butylacrylamide[1]

BY N. C. DENO, TOM EDWARDS AND CARL PERIZZOLO

The kinetics of the acid-catalyzed formation of N-*t*-butylacrylamide from *t*-butyl alcohol and acrylonitrile have been studied from 20–69% sulfuric acid. The rate is proportional to the first powers of the acrylonitrile concentration, the *t*-butyl alcohol concentration and the Hammett h_0 function. The rate constants for the reactions of protonated *t*-butyl alcohol with water, acrylonitrile and propionitrile were found to be identical within a factor of three. The combined results are interpreted in terms of transition states in which the incoming group is so weakly bonded to the transition state that its nature has only a small effect on the rate. The results do not support the concept of a free *t*-butyl cation. The rate of hydrolysis of acrylonitrile was studied from 28–85% sulfuric acid. The rate is proportional to the concentration of acrylonitrile and the h_0 function.

Since Whitmore[2] first introduced the concept of aliphatic cations, considerable controversy has existed as to their exact nature.

On the basis that methanolysis of hydrogen 2,4-dimethylhexyl-4-phthalate proceeded with 55% inversion and 45% racemization, Doering and Zeiss[3] concluded that no free alkyl cation was an intermediate. Their argument was that if the *t*-alkyl cation was not free enough to racemize, it is difficult to conceive of a transition state in which there is no covalent participation by the incoming group. Their conclusion is strongly supported by the failure to observe a mass-law effect in the solvolysis of *t*-alkyl halides.[4]

The strongest arguments proposed in favor of free *t*-alkyl cations are the studies of Winstein, Grunwald and Jones[5] on the variation of rate with solvent. We interpret these studies as showing that there is nearly complete charge separation in the transition state, a situation that can be accommodated by transition states of the type described by Doering and Zeiss.

In our work, a study of the acid-catalyzed reactions of *t*-butyl alcohol was initiated with the expectation that it would provide evidence as to the existence of the *t*-butyl cation as a reaction intermediate. It was first necessary to develop acidity function theory and this was the concern of an earlier paper.[6]

The reaction chosen for study was the formation of N-*t*-butylacrylamide from *t*-butyl alcohol and acrylonitrile. This reaction is of a type extensively studied by Ritter,[7] who demonstrated that it was a remarkably general reaction between alcohols and nitriles.

Experimental

Extinction Coefficients.—In order to determine the concentration of N-*t*-butylacrylamide spectroscopically, it was necessary to know the extinction coefficients for *t*-butyl alcohol and acrylonitrile (the reactants), N-*t*-butylacrylamide (the product), acrylamide (a side product) and acrylic acid (the hydrolysis product of acrylamide or N-*t*-butylacrylamide). The *t*-butyl alcohol and acrylonitrile showed no measurable absorption in the region of wave lengths greater than 220 mμ at the concentrations employed in the kinetic runs. Their absorptions were thus neglected. The absorption spectra of the remaining compounds are summarized in Table I.

Kinetic Measurements.—The kinetics of the reaction between *t*-butyl alcohol and acrylonitrile were studied in 20–69% sulfuric acid. The formation of the product, N-*t*-butylacrylamide, was determined spectroscopically with a Beckman DU spectrophotometer. Measurements were made at 260–280 mμ. The cells of the spectrophotometer were thermostated at 25 ± 0.1° by means of thermospacers. Rapid runs were conducted entirely in the spectrophotometer cells whereas slow runs were held in thermostated volumetric flasks from which a portion was periodically introduced into the cells.

(1) Grateful acknowledgment is made of the support of this research by a grant from the Petroleum Research Fund of the American Chemical Society.

(2) F. C. Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

(3) W. E. Doering and H. Zeiss, THIS JOURNAL, **75**, 4733 (1953).

(4) L. Bateman, M. Church, E. Hughes, C. Ingold and N. Taher, *J. Chem. Soc.*, 979 (1940). Note comments of J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1956, pp. 103–105.

(5) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); S. Winstein, E. Grunwald and N. W. Jones, *ibid.*, **73**, 2700 (1951).

(6) N. Deno and C. Perizzolo, *ibid.*, **79**, 1345 (1957).

(7) J. Ritter and co-workers, *ibid.*, **70**, 4045, 4048 (1948); **71**, 4128, 4130 (1949); **73**, 4076 (1951); **74**, 763 (1952).

TABLE I

ABSORPTION SPECTRA OF N-t-BUTYLACRYLAMIDE, ACRYL-
AMIDE AND ACRYLIC ACID IN 41 AND 55% SULFURIC ACIDS

Wave length (mμ)	N-t-Butyl-acrylamide	Extinction coefficient[a]			
		Acrylamide		Acrylic acid	
225		3340	4290	373	418
230		1660	1990	217	222
235		770	755	146	147
240	2700	360	355	104	109
250	840	872	90	86	63	70
260	169	164			30	37
270	27	22				

[a] Under each compound, the values in the first column are for 41% sulfuric acid and those in the second column are for 55% acid.

All runs were conducted as pseudo first-order reactions by using at least tenfold excess of either reactant, acrylonitrile or t-butyl alcohol. The fit of the data with first-order kinetics is demonstrated in Table II for two typical runs in which t-butyl alcohol was in excess and a run in which acrylonitrile was in excess.

TABLE II

DEMONSTRATION OF FIRST-ORDER KINETICS FOR FORMATION OF N-t-BUTYLACRYLAMIDE AT 30.0 AND 69.1% H_2SO_4 WITH EXCESS t-BUTYL ALCOHOL AND AT 41.0% H_2SO_4 WITH EXCESS ACRYLONITRILE

% Completion	Time (days)	Optical[a] density, 260 mμ	$k \times 10^6$, l. mole^{-1} sec.$^{-1}$
30.0% H_2SO_4, $c_{t-buOH}/c_{RCN} = 11.7$			
0	0	0	
10	2.60	.300	2.24
20	5.40	.600	2.29
30	8.70	.900	2.27
40	12.30	1.200	2.30
50	16.70	1.500	2.30
60	22.2	1.800	2.29
70	29.6	2.10	2.26
80	39.3	2.40	2.27
85.7	45.3	2.57	2.37
100		3.00	
69.1% H_2SO_4, $c_{t-buOH}/c_{RCN} = 11.7$			
Time (min.)			
0	0	0	
10	14.5	.300	580
20	31.0	.600	575
30	50.0	.900	570
40	71.5	1.200	571
100		3.00	
41.0% H_2SO_4, $c_{t-buOH}/c_{RCN} = 0.0715$			
Time (hr.)			
0	0	0	
10	56	.042	14.4
20	117	.085	14.5
30	183	.127	14.8
40	265	.169	14.7
50	360	.222	14.6
60	490	.254	14.2
70		.296	
80		.338	
100		.423	

[a] The values are taken from a smooth curve drawn through a plot of optical density against time. Observations at 270 and 280 mμ were converted to the equivalent at 260 mμ. The value at 100% completion was calculated from the extinction coefficient of the product, N-t-butylacrylamide, and the initial concentrations of reactants.

The rate constants, which are summarized in Table III, were calculated from integrated forms of the equation $dc_{product}/dt = kc_{RCN} c_{t-BuOH}$. The added t-butyl alcohol significantly lowered the acidity of the reaction mixtures similar to the effect of adding 2-propanol to water–sulfuric acid.[8] It was necessary to make small corrections for this effect in computing the rate constants since varying concentrations of t-butyl alcohol were used in different runs. For this purpose the Hammett H_0 function[9] was measured as a function of added t-butyl alcohol at several concentrations of sulfuric acid. The data are summarized in Table IV. The method of computing the correction for k was to determine d log k/dH_0 at each % H_2SO_4 from the variation of rate with % H_2SO_4. The change in log k due to the added t-butyl alcohol could then be estimated from the data in Table IV.

TABLE III

RATE CONSTANTS FOR THE FORMATION OF N-t-BUTYL-ACRYLAMIDE

Run	% H_2SO_4	Initial molarities CH$_2$=CHCN	t-BuOH	$(k \times 10^6)$,[a] l. mole^{-1} sec.$^{-1}$	% Completion[b]
1	20.0	0.0178	0.209	0.49	25
2	25.0	.0178	.209	1.15	60
3	30.0	.0178	.209	2.58	80
4	35.0	.0178	.209	4.48	80
5	37.0	.0178	.209	7.05	70
6	39.0	.0178	.209	8.15	90
7	41.0	.0178	.209	13.4	60
8	41.0	.0175	.410	12.7	5
9	41.0	.0356	.00255	12.6	50
10	45.3	.0178	.209	22.9	30
11	49.5	.0178	.209	53.6	8
12	54.8	.0178	.209	98.8	15
13	54.8	.0175	.410	98.2	25
14	54.8	.0356	.209	91.3	13
15	55.3	.0178	.209	103	30
16	57.3	.0178	.209	140	15
17	57.3	.0356	.00255	126[c]	85
18	59.5	.0178	.209	182	13
19	61.3	.0178	.209	191	25
20	62.8	.0178	.209	220	15
21	64.4	.0178	.209	274	30
22	64.9	.0178	.209	350	20
23	65.8	.0178	.209	488	25
24	68.0	.0178	.209	560	30
25	69.1	.0178	.209	628	40

[a] The values of k were calculated from integrated forms of the equation $dc_{amide}/dt = kc_{RCN}c_{t-BuOH}$. The concentrations used in this equation were the stoichiometric concentrations. All values of k were corrected for the small change in acidity due to the added t-butyl alcohol. [b] The rate constants did not vary by more then 10% out to the % completion listed in this column. The runs at 20 and 25% H_2SO_4 were inconveniently slow to carry to completion. The runs at 40–50% acid were arbitrarily stopped at the % completion listed. For runs at acid concentrations greater than 50%, no observations were made beyond the % completion listed in this column because of the appearance of cloudiness. [c] In this run where the acrylonitrile was in excess, about 17% of the t-butyl alcohol disappeared in some reaction other than the formation of N-t-butylacrylamide as judged by the final constant optical density reading. When a correction was made based on the assumption that the side reaction involved a bimolecular reaction between two derivatives of t-butyl alcohol, the calculated values of k were constant within 10% out to 85% completion. For these reasons this value of k must be considered uncertain.

Evidence for the Validity of the Kinetic Data.—Although Ritter[7] has shown that under certain conditions acryloni-

(8) P. D. Bartlett and J. D. McCollum, THIS JOURNAL, 78, 1441 (1956).

(9) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter IX.

TABLE IV

VARIATION IN H_0 ON ADDITION OF t-BUTYL ALCOHOL TO FOUR DIFFERENT CONCENTRATIONS OF SULFURIC ACID

Ml of t-butyl alcohol per l. of soln.	A	B	C	D
			$H_0{}^a$	
0	1.28	0.31	−0.92	−4.36
10	1.30	.32		
20	1.36	.36	− .86	−4.32
40	1.46	.40	− .78	−4.26
60	1.54	.44		
80	1.58	.46		
100	1.63	.51		

[a] The data in column A refer to addition of t-butyl alcohol to a 0.45% solution of sulfuric acid, column B to 4.39% acid, column C to 20.35% acid and column D to 60.3% acid. The indicators used were 2-nitroaniline at 0.45 and 4.39% acid, 4-chloro-4-nitroaniline at 20.35% acid and 2,4-dinitroaniline at 60.3% acid.

trile and t-butyl alcohol react to give high yields of N-t-butylacrylamide, it was necessary to demonstrate that this was true under the conditions of the kinetic experiments. Related to this problem was the fact that both reactants and the product undergo hydrolysis or dehydration–polymerization in at least some of the regions of acidity studied. Particular emphasis was thus placed on demonstrating that the spectrophotometer data really measured the formation of N-t-butylacrylamide and that its formation was nearly quantitative.

The most direct evidence was that crystalline N-t-butylacrylamide was isolated in runs at 41 and 55% sulfuric acids in amounts equal to 80% of that calculated from the rate data.

The side reactions, hydrolysis of acrylonitrile and N-t-butylacrylamide, were investigated independently. Both of these reactions were found to be sufficiently slow under the conditions employed so that they did not interfere with measurements on the formation of N-t-butylacrylamide.

The behavior of t-butyl alcohol alone in the various concentrations of sulfuric acid was investigated spectroscopically to be certain that no significant absorption due to isobutene polymers or oxidation products was present during the time that the kinetic data were recorded. The behavior of the t-butyl alcohol in the various concentrations of sulfuric acid also was observed visually to see whether any cloudiness developed. No measurements were taken after any cloudiness developed.

The most convincing evidence was the spectrophotometric measurements. Below 45% sulfuric acid where formation and polymerization of isobutene was absent, the final optical density reading was generally at least 95% of that calculated for complete conversion of the reactants to the product, N-t-butylacrylamide. The calculated values were based on the extinction coefficient of the product (Table I) and the initial concentrations of reactants. In addition the calculated values of the rate constant, k, were constant until either the reaction was complete or cloudiness prevented further measurements.

Hydrolysis of Acrylonitrile to Acrylamide.—The rate of formation of acrylamide from acrylonitrile was determined from 25–85% H_2SO_4. The concentration of acrylamide was followed by measurements of the optical density at 230–250 mμ. The further hydrolysis of acrylamide to acrylic acid was sufficiently slow so that it did not interfere.

The rate constants, k, were calculated from the integrated form of the equation $-dc_{RCN}/dt = kc_{RCN}$. In all cases values of k were constant to within 5% at all stages of the reaction. The data are summarized in Table V.

Competition Experiments.—The relative rate of reaction of t-butyl alcohol with acrylonitrile and propionitrile was determined at 50.3% H_2SO_4. The initial concentrations were made sufficiently large so that the first-order direct hydrolysis of acrylonitrile did not interfere. Although no direct measurements were made on the rate of hydrolysis of propionitrile, this reaction was slow enough so as not to interfere. The evidence for this was that the ratio of rates was constant although the ratio of initial concentrations of the two nitriles was varied from 2.42/1 to 0.58/1. The data are summarized in Table VI.

TABLE V

RATE CONSTANTS AND THEIR VARIATION WITH SULFURIC ACID CONCENTRATION FOR THE HYDRATION OF ACRYLONITRILE TO ACRYLAMIDE

% H_2SO_4	$k \times 10^9$, sec.$^{-1}$	% Completion[a]	$\dfrac{d \log k}{d \% H_2SO_4}$	$\dfrac{-dH_0}{d \% H_2SO_4}$	$\dfrac{d \log c_{H_3O}+}{d \% H_2SO_4}$
25.5	4.27	0.5	0.04	0.065	0.021
41.3	22.2	5	.061	.087	.013
54.8	188	40	.078	.110	.010
72.0	5960	90	.112	.124	
85.0	82800	90	.112	.134	

[a] The runs were arbitrarily stopped at the % completion listed in this column.

TABLE VI

RELATIVE RATES OF REACTION OF t-BUTYL ALCOHOL WITH ACRYLONITRILE AND PROPIONITRILES IN 50.3% H_2SO_4

t-Butyl alcohol	Acrylonitrile	Propionitrile	Caled.[a]	Obsd.	$k_{propionitrile}[b]$ / $k_{acrylonitrile}$
	Initial molarities		Final optical[a] density		
0.102	0.184	0.304	16.9	4.43	1.78
.109	.171	.295	18.1	4.87	1.72
.111	.227	.225	18.4	6.92	1.90
.093	.128	.130	15.4	5.67	1.97
.100	.377	.156	16.6	9.00	2.02

[a] The calcd. values were obtained by assuming that the t-butyl alcohol was completely converted to N-t-butylacrylamide. The observed values were obtained by multiplying the optical density of diluted reaction mixtures by the dilution factor. [b] The calculation of this ratio was made by the equivalent of a graphical integration which took into account that the ratio of the concentrations of the two nitriles changed during the course of the reaction and that the two nitriles disappeared at different rates.

Discussion

Rate Law for the Formation of N-t-Butylacrylamide.—At constant concentration of sulfuric acid, the rate law was found to be eq. 1. The majority of reactions were conducted

$$dc_{amide}/dt = kc_{RCN}c_{t-buOH} \qquad (1)$$

using an 11.7/1 ratio of t-butyl alcohol concentration to acrylonitrile concentration. In these runs, the rate constant calculated by eq. 2 was constant (Table II) to within 10% out to the % completions listed in Table III.

$$k = (2.3)(\log c_{RCN}/c'_{RCN})/(c_{t-buOH})(t) \qquad (2)$$

This demonstrated that the rate was proportional to the first power of the acrylonitrile concentration.

The proportionality of the rate to the first power of the t-butyl alcohol concentration was demonstrated in two ways. First, when the concentration of t-butyl alcohol was doubled (runs 8 and 13), the value of k was unchanged providing that it was computed by eq. 2. Secondly, in two runs (runs 9 and 17, Table III) the procedure was reversed in that a 14/1 excess of acrylonitrile was employed. In run 9 the plot of log c_{t-buOH} against time was linear. This was also true for run 17 providing a correction (cf. footnote c, Table III) was made for the 17% of the t-butyl alcohol which disappeared by an uninvestigated side reaction.

In summary, eq. 1 was obeyed over a 330-fold variation in the ratio of t-butyl alcohol concentration to acrylonitrile concentration. This range probably could have been extended greatly by using lower acrylonitrile concentrations, but exten-

sion in this direction was not critical to the arguments to be considered.

From 20–40% sulfuric acid, the variation of rate with acid concentration was expressed accurately by eq. 3 as shown by the data in Table VII. In this eq. as with all others that follow in this paper, all derivatives are taken in respect to % H_2SO_4 unless otherwise specified. Thus d log k stands for d log k/d % H_2SO_4.

$$d \log k = -dH_0 \qquad (3)$$

TABLE VII

VARIATION OF RATE CONSTANTS WITH SULFURIC ACID CONCENTRATION FOR THE FORMATION OF N-*t*-BUTYL-ACRYLAMIDE

% H_2SO_4	$\dfrac{d \log k}{d \% H_2SO_4}$	$\dfrac{d \log k'^a}{d \% H_2SO_4}$	$\dfrac{-dH_0}{d \% H_2SO_4}$	$\dfrac{-dC_0}{d \% H_2SO_4}$
20	0.068	0.068	0.068	0.12
25	.068	.068	.065	.13
30	.068	.068	.068	.14
35	.068	.068	.074	.16
40	.068	.072	.084	.16
45	.066	.081	.096	.18
50	.062	.091	.106	.20
55	.061	.102	.110	.23
60	.060	.120	.110	.26
65	.060	.170	.116	.26

[a] The calculation of k' differed from that of k in that instead of using the stoichiometric concentration of *t*-butyl alcohol in eq. 2, a concentration of *t*-butyl alcohol was used which was corrected for the equilibrium between alcohol and protonated alcohol. This correction was calculated on the hypothesis that $pK = -3.8$ for *t*-butyl alcohol. It was not felt necessary to tabulate values of k'.

From 40–70% sulfuric acid the variation became more complex. This was anticipated because Bartlett and McCollum have found that ethanol has $pK = -2.2$,[10] which means that it is half-protonated in 40% H_2SO_4. For 2-propanol, $pK = -3.2$,[8] which means that it is half-protonated in 50% H_2SO_4. It was thus expected that *t*-butyl alcohol would be half-protonated near 60% H_2SO_4, and that this protonation of the alcohol would affect the fit of the kinetics with eq. 3.

If a $pK = -3.8$ ($H_0 = -3.8$ at 55% H_2SO_4) is assumed for *t*-butyl alcohol and the concentration of free *t*-butyl alcohol computed on this basis, the kinetic data now fit eq. 2 from 20–65% H_2SO_4 as shown in Table VII. The fit is not sensitive to the value chosen for the pK so that the value -3.8 must be considered at best an estimate precise to perhaps ±0.4.

The complete rate eq. is thus given by eq. 4 where h_0 is the $-$antilog H_0.

$$dc_{amide}/dt = kc_{RCN}c_{t-BuOH} h_0 \qquad (4)$$

Significance of Eq. 3.—On the basis of limited work, there appear to be two groups of cations for which d log f in sulfuric acid is dependent only on the sulfuric acid concentration.[6] The first group are cations of a type (type I) exemplified by Ar_3C^+, $(C_6H_5)_4P^+$ and Bu_4N^+ in which the common character is a positive charge well shielded by non-polar groups. The second group are cations of the general formula BH^+ (type II) where the common character is a positive charge on the periphery of a non-polar moiety.

(10) Unpublished results.

By the development previously presented,[6] the fact that the data fit eq. 3 and 4 would be interpreted to mean that the transition state resembles type II, BH^+, close enough so that d log (f_{BH^+}/f^*) is negligible. Generally this would be more likely to happen if the transition state were composed of acrylonitrile and protonated *t*-butyl alcohol rather than some other derivative of *t*-butyl alcohol (such as the *t*-butyl cation) and this is our tentative interpretation.

Relative Rates of Reaction.—In a typical SN1 reaction involving a stable cation intermediate such as the triphenylmethyl cation, the relative rate of formation of triphenylmethyl azide and triphenylmethanol is 2.8×10^5.[11] The wide range of rate constants in SN2 reactions is too well known to merit examples. In contrast, a unique feature of the substitution reactions of *t*-butyl derivatives is that their rate constants are so similar.

Using the data of Ingold, *et al.*, Swain, Scott and Lohmann[11] calculated the relative rate of formation of *t*-butyl azide to the rate of formation of *t*-butyl alcohol (from the solvolysis of *t*-butyl chloride in 10% water–90% acetone at 50°) as being 3.9.

Another example of similar rates is the ratio of *t*-butyl thiocyanate to *t*-butyl isothiocyanate formed in solvolysis of *t*-butyl chloride in the presence of thiocyanate ions. Taft and Cannell[12] found the ratio to be 71/29 at 38°. The same authors found that the ratio of the same products was 65/35 when *t*-butylamine was treated with nitrous acid in the presence of thiocyanate ion.[12]

In our work we found that the relative rates of reaction of propionitrile and acrylonitrile with *t*-butyl alcohol in the acid-catalyzed Ritter reaction was 1.9/1 (Table VI).

A more striking example is a comparison of the rates of oxygen exchange on *t*-butyl alcohol with the rate of reaction of acrylonitrile with *t*-butyl alcohol. Dostrovsky and Klein[13] measured the oxygen exchange rate. Their data at 55 and 75° in 0.45 M H_2SO_4 and one molar *t*-butyl alcohol can be extrapolated to 25° to give a rate constant equal to 2.42×10^{-7} sec.$^{-1}$. If this reaction is assumed to be of the same type as the formation of N-*t*-butylacrylamide, the rate constant must be divided by the molarity of water (about 51 M) to reduce the rate constant to that for unit concentration of water and *t*-butyl alcohol. The rate constant then becomes 4.8×10^{-9} 1. mole^{-1} sec.$^{-1}$. This rate constant can be compared with the rate constant, $k = 1.7 \times 10^{-9}$ 1. mole^{-1} sec.$^{-1}$, calculated for the formation of N-*t*-butylacrylamide at the same value of H_0 ($H_0 = 1.60$ for 0.45 M H_2SO_4 and 1 M *t*-butyl alcohol). The relative rates are 2.8/1 and this is interpreted to mean that the protonated *t*-butyl alcohol reacts 2.8 times as fast with water as with acrylonitrile. With propionitrile, water reacts about 1.4 times as fast.

The similarity in rates in itself could be interpreted as due to an unstable cation intermediate which is not selective in its reactions or it could

(11) C. G. Swain, C. B. Scott and K. H. Lohmann, THIS JOURNAL, **75**, 136 (1953).

(12) Ph.D. Thesis of L. G. Cannell, Pennsylvania State Univ., 1956.

(13) I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 791 (1955).

equally well be interpreted as due to weak bonding of the incoming group which thus has a relatively small effect on the free energy of the transition state. The latter interpretation is more in accord with eq. 4 and the experiments of Doering and Zeiss.[3]

These results on t-butyl alcohol make it probable that the oxygen exchanges on 2-butanol are simple displacements on the protonated alcohol by water. The result that each exchange proceeds with inversion[14] is thus a most natural result. The author's conclusion that water was not covalently bonded to the transition state was based on the Hammett-Zucker hypothesis which is now suspect.[6]

It is of interest that substitution reactions of even triphenylmethyl derivatives become displacement reactions in non-ionizing media.[15] In these circumstances, the reactions are like those of the t-butyl derivatives discussed above in that the rate shows little variation with the nature of the incoming group.[16] It is hard to see how these reactions can proceed in any other way than with in-

(14) C. A. Bunton, A. Konasiewicz and D. R. Llewellyn, *J. Chem. Soc.*, 604 (1955).

(15) C. G. Swain, THIS JOURNAL, **70**, 1121 (1948); C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

(16) D. Cram and F. Hawthorne, *ibid.*, **76**, 3451 (1954).

version of configuration and we are currently studying this problem.

Although we have interpreted the reactions of t-butyl derivatives as an extreme type of displacement reaction (S_N2), some of the characteristics closely resemble those of an ideal S_N1 reaction. Thus the rates depend primarily on the structure of the t-alkyl group and may parallel the cation stability as has been shown for solvolysis of diarylmethyl derivatives.[17] Also the large charge separation in the transition state will cause the variation of rate with media to be similar to that found for an ideal S_N1 reaction. This intermediate type of nucleophilic displacement reaction as exemplified by the substitution reactions on t-butyl alcohol have a unique character of their own and it may be convenient to term them S_N(int.) reactions.

Hydrolysis of Acrylonitrile to Acrylamide.—The data in Table V show that to within 10–30% d log $k = -dH_0$. The transition state contains acrylonitrile and a proton. The presence or absence of water is undecided.

Acknowledgment.—We wish to acknowledge discussions with Dr. R. W. Taft, Jr.

(17) N. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955).

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The Binding of Ions to the Muscle Proteins. Measurements on the Binding of Potassium and Sodium Ions to Myosin A, Myosin B and Actin[1,2]

BY M. S. LEWIS AND H. A. SAROFF

The binding of sodium and potassium ions to myosin A, myosin B, actin and bovine and human serum albumin was studied using electrodes made of collodion membranes which were permselective to cations. Data showing pH dependence, concentration dependence and temperature dependence were obtained. It was found that myosin A and myosin B bound sodium and potassium, but that the other proteins did not. The imidazol and amino groups appear to control the binding of sodium and potassium to myosin A and B. The values of the equilibrium constants for the interaction of sodium and potassium with the myosins were determined, and values for ΔF° and ΔH°, were calculated.

Introduction

The interaction of potassium and sodium ions with the proteins of muscle is undoubtedly of considerable importance in the contractile processes in muscle. The extent of these interactions has been studied by several investigators by measuring the amount of the ion adsorbed by threads of myosin.[3-6] Their data present certain difficulties in interpretation because the threads represent a phase different from that of the solution in which they were equilibrated. This study was carried out on the

viscous solutions and suspensions of the muscle proteins rather than on the precipitated thread. Other evidence for sodium and potassium ion binding to myosin can be found in Mihalyi's[7] hydrogen ion titration data at different salt concentrations.

When a suitable electrode exists for a certain ion, it is possible to determine the extent of the interaction of that ion with a protein by determining the activity of the ion in the presence of the protein. Hydrogen ion interactions with proteins have been studied using the hydrogen and glass electrodes. Scatchard, Scheinberg and Armstrong[8] studied the binding of chloride to serum albumin using silver–silver chloride electrodes. Carr has used permselective membranes as membrane electrodes to study the binding of cations and anions to a wide variety of proteins.[9]

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(2) Presented before the American Physiological Society at the 40th Annual Meeting of the Federation of American Societies for Experimental Biology, April 17, 1956, Atlantic City, N. J.

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