[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE RELATIONSHIP OF THE CONSTITUTION OF CERTAIN ALKYL HALIDES TO THE FORMATION OF NITROPARAFFINS AND ALKYL NITRITES

BY ROBERT B. REYNOLDS AND HOMER ADKINS

RECEIVED AUGUST 30, 1928 PUBLISHED JANUARY 8, 1929

The reaction of alkyl halides with metallic nitrites results in the formation of varying proportions of the isomeric nitroparaffins and alkyl nitrites. It has been shown by various investigators that the ratio of the isomers in the reaction mixture is dependent upon the nature of the particular alkyl radical and metal used.[1]

Despite the very considerable interest in the subject, as shown by the list of publications, there has been no systematic or accurate determination of the proportions of isomers produced in the reaction of any extensive list of reagents. A summary of the previous observations made upon the reactions of various alkyl halides with silver nitrite is given in Table I.

TABLE I

FORMATION OF ALKYL NITRITES AND NITROPARAFFINS FROM VARIOUS ALKYL HALIDES WITH SILVER NITRITE

Alkyl halides	Yield of isomers, %	Nitro-paraffin, %	Alkyl nitrite, %	Observers
Methyl iodide	?	90	None	Meyer and Stuber
Methyl iodide	63	52.6	47.4	Ray and Neogi
Ethyl iodide	?	"50"	"50"	Meyer and Stuber
Ethyl iodide	83	52.9	47.1	Ray and Neogi
n-Propyl iodide	?	Mainly	?	Meyer and Rilliet
*Iso*propyl iodide	80.7	44.1	55.9	Ray and Neogi
Allyl iodide	Poor	?	?	Meyer and Chojnacki
Allyl bromide	34	Mostly	Small	Schiff
Allyl bromide	?	Mostly	Small	Brackebusch
n-Butyl iodide	?	53	?	Züblin
*Iso*butyl iodide	?	"50"	"50"	Demole
Sec.-butyl iodide	58	?	?	Meyer and Locher
Tert.-butyl iodide	?	Small	Mainly	Tscherniak
Iso-amyl iodide	34.7	79.5	20.5	Ray and Neogi

The present investigation was undertaken in order to ascertain the facts with regard to the proportion of isomers formed from various alkyl halides and silver nitrite, in the hope that ultimately some light would

[1] (a) V. Meyer, Stuber, Rilliet and Chojnacki, *Ann.*, **171**, 1 (1872); (b) V. Meyer and Locher, *ibid.*, **180**, 134 (1876); (c) V. Meyer and Stuber, *Ber.*, **5**, 203, 399 (1872); (d) V. Meyer and Rilliet, *ibid.*, **5**, 1032 (1872); (e) V. Meyer and Chojnacki, *ibid.*, **5**, 1037 (1872); (f) Tscherniak, *Ann.*, **180**, 155 (1876); (g) Ray and Neogi, *Proc. Chem. Soc.*, **23**, 246 (1907); (h) Demole, *Ann.*, **175**, 142 (1874); (i) Eichler, *Ber.*, **12**, 1883 (1879); (j) Brackebusch, *ibid.*, **7**, 225 (1874); (k) Schiff, *ibid.*, **7**, 1141 (1874); (l) Züblin, *ibid.*, **10**, 2083 (1877).

be shed upon the relationship between the constitution of the reactants and the relative rates of the simultaneous reactions.

Preparation of Alkyl Halides.—*n*-Propyl, *iso*propyl, *n*-butyl and *iso*butyl iodides were prepared through the reaction of the corresponding alcohol with a mixture of red and white phosphorus and iodine as described by Adams, Kamm and Marvel.[2] It was found that a better product was obtained in the case of *sec.*-butyl iodide if the older method of adding iodine to red phosphorus contained in the alcohol was used. The method of Norris[3] was used for the preparation of *tert.*-butyl iodide and that of Freunder and Damond[4] for the preparation of cyclohexyl iodide. The sodium bromide method[5] was used for the preparation of *n*-propyl and *n*-butyl bromide. The method of Norris[6] was used for the preparation of *sec.*-propyl bromide. *Iso*butyl, *sec.*-butyl, *tert.*-butyl, *iso*-amyl, *n*-heptyl and *sec.*-octyl bromides were prepared through the reaction of the corresponding alcohol with phosphorus tribromide. The latter was prepared by the method of Schorlemmer.[7] In the preparation of the alkyl halide the tribromide was allowed to drop slowly into the alcohol held in an ice-bath. The reaction mixture was allowed to stand for an hour or so after the addition of the last of the tribromide and then gently warmed. The halide was then separated, washed with water (then with sulfuric acid in the case of *iso*butyl bromide) then with a 10% solution of sodium carbonate and repeatedly with water. The product was dried over calcium chloride and fractionated. The yields were from 80 to 85% of the theoretical. Benzyl bromide was prepared through the reaction of the alcohol with constant boiling hydrobromic acid in the molecular ratio of 1:3. The yield was 92%. Allyl and β-phenylethyl bromide were obtained from the Eastman Kodak Company.

Reaction of Silver Nitrite with Various Alkyl Halides.—The reaction of an alkyl halide with silver nitrite was in general carried out as by Victor Meyer except that the silver nitrite was not mixed with sand. The desired amount of silver nitrite was placed in a round-bottomed flask which was connected by a ground-glass joint to a dropping funnel and a spiral condenser. The alkyl halide was then slowly dropped onto the nitrite, the flask being cooled in an ice–salt mixture. If the reaction was too rapid, more or less decomposition took place with the evolution of oxides of nitrogen. The reaction mixture was allowed to stand for two or three hours in the ice-bath after the addition of the last of the alkyl halide. The mixture was then gently refluxed in a water or oil-bath for four or five hours. The mixture of alkyl nitrite and nitroparaffin was removed from the reaction mixture by distillation, first at atmospheric and then under reduced pressure. If the distillate showed a test for a halide (as it usually did), the mixture was refluxed with a further quantity of silver nitrite. The distillate from this second treatment with silver nitrite was analyzed for nitrogen by the Dumas method. If the result of this analysis indicated that the distillate was a pure mixture of the isomeric alkyl nitrite and nitroparaffin, the mixture was analyzed as described below for the percentage of nitroparaffin.

In the case of one of each of the two preparations from *n*-butyl iodide, *n*-propyl and *n*-heptyl bromide, the method was changed in that the silver nitrite was slowly added

[2] Adams, Kamm and Marvel, "Organic Chemical Reagents," University of Illinois Bulletin, Urbana, **1919**, Vol. I, p. 19.

[3] Norris, *Am. Chem. J.*, **38**, 641 (1907).

[4] Freunder and Damond, *Compt. rend.*, **141**, 593 (1905).

[5] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1**, 6 (1921).

[6] Norris, ref. 3, p. 640.

[7] Roscoe and Schorlemmer, "Treatise on Chemistry," Macmillan Co., New York, **1920**, Vol. I, 5th ed., p. 649.

(two to three hours) with shaking to the alkyl halide. This modification in the procedure had no effect upon the yield or proportion of the isomers formed. This procedure was used in both of the preparations for *sec.*-octyl bromide, *tert.*-butyl bromide and allyl bromide. In the case of the first of these the reaction mixture was not refluxed but merely heated to 120–125° for two or three hours. *Tert.*-butyl bromide at first reacted rather slowly with silver nitrite but after a little had reacted the reaction became so vigorous that ten hours was consumed in adding 60 g. of silver nitrite. Allyl bromide was so reactive that it was necessary to add the 35 g. of silver nitrite in very small portions during an interval of twenty hours.

The distillates from the reactions of *tert.*-butyl iodide and cyclohexyl iodide with silver nitrite represented yields of less than 50% of the theoretical amount. The determination of nitrogen showed that these distillates were very far from being a mixture of only the nitro compound and the nitrite. Rather considerable amounts of benzaldehyde were formed in the reaction of benzyl and β-phenylethyl bromides. Attempts to purify the mixture of isomers from the benzaldehyde were unsuccessful. The reaction products of these four alkyl halides therefore were not analyzed for nitroparaffins.

Analysis of Reaction Mixtures.—All previous investigators have attempted to determine the proportion of the isomers in the reaction product by fractional distillation, but in this case a more accurate method was desired. Various methods were rather thoroughly examined and discarded for one reason or another before an accurate but laborious method of analysis was adopted. Attempts were made to saponify the ester and determine the nitrous acid through its reaction with urea to form carbon dioxide and nitrogen. Attempts were also made to titrate the nitrous acid in the presence of the nitroparaffin. Attempts also were made to determine the nitrous acid iodometrically, but all of these methods failed to give accurate results when used for the analysis of mixtures.

The method finally adopted for the analysis involved the addition of an *alcoholic* solution of sodium hydroxide to a weighed sample of a mixture of isomers. The salt of the nitro compound was thereby formed and the alkyl nitrite saponified. The solution was then evaporated and the residue, consisting of the sodium salt of the nitro compound and sodium nitrite, analyzed by a wet combustion method for carbon. From these data it is possible to calculate the percentage of nitro compound in the mixture of isomers.

The apparatus used for the analysis was arranged as follows.[8] A supply of pure oxygen was led into the top of a 125-cc. dropping funnel whose stem passed through a ground-glass joint to the bottom of a 300-cc. Kjeldahl type of flask. A tube led from the top of this flask through a spiral condenser to a U-tube filled with pumice and chromic anhydride. The products of combustion then passed through two U-tubes containing glass wool plugs saturated with anhydrous sulfuric acid and a layer of acid partially filling the space at the bottom of the U. The gases then passed into a combustion tube supported in a gas furnace. Copper oxide was placed for a length of 5 inches in

[8] White and Holben, *Ind. Eng. Chem.*, **17**, 83 (1925); Desgrez and Venario, *Compt. rend.*, **180**, 886 (1925).

the center of the tube, while reduced copper spirals were placed on each side. After leaving the combustion furnace, the gases passed through two sulfuric acid drying tubes and then into a Geissler potash bulb properly provided with guard tubes containing soda lime and calcium chloride.

The procedure for the analysis of the mixture of isomers was as follows. A sample of from 0.15 to 0.5 g. was weighed into previously weighed, thin-walled glass vials and immediately sealed off. The vial was placed in the combustion flask and 10 cc. of a 0.1 *N* alcoholic solution of carbonate-free sodium hydroxide added. (The latter was prepared from absolute alcohol and sodium hydroxide.) The vial was broken and the mixture allowed to stand for a few minutes. The volatile material was then removed by distillation from a bath, first at atmospheric pressure until all the visible liquid had distilled, and then under a pressure of a few millimeters. It was found necessary to take great care at this point in order to prevent spattering. The temperature was finally raised to 135–140° during three or four hours. In the case of the heptyl and octyl compounds the temperature was raised to 180° for an hour or two and then maintained at 155° overnight.

After the volatile material was thus expelled, the combustion flask was attached to the rest of the combustion apparatus. Ten to 15 cc. of a chromic acid solution (100 g. of chromic anhydride in 200 cc. of water) was then added under a slight pressure of oxygen followed by 100 cc. of sulfuric acid which had been previously boiled for two hours. Fifteen to 20 cc. of the acid was allowed to remain in the dropping funnel during the combustion. The combustion flask was slowly heated with a Bunsen burner so that there was a steady flow of gas into the potash bulb. Finally the oxidation mixture was boiled for a few minutes. After the flask had cooled somewhat, the system was swept out with a slow stream of purified oxygen. A correction was applied of 0.0327 g. of carbon dioxide.

That the method gives reasonably accurate results is shown by the results of analyses carried out on pure nitrobutane and mixtures of it with *n*-butyl nitrite. Representative analyses are given in Table II.

TABLE II

ANALYSES FOR NITROBUTANE IN MIXTURES WITH *n*-BUTYL NITRITE

$C_4H_9NO_2$, present, g.	C_4H_9ONO, present, g.	$C_4H_9NO_2$, found, g.	$C_4H_9NO_2$, present, %	$C_4H_9NO_2$, found, %
0.4855	None	0.4834	100	99.57
.1147	None	.1140	100	99.39
.4475	None	.4480	100	100.11
.1201	None	.1195	100	99.40
.1683	None	.1665	100	99.75
.1722	0.6370	.1778	21.28	21.96
.1768	1.3543	.1752	11.54	11.42
.2181	1.2920	.2242	14.44	14.84
.2467	0.2107	.2452	53.98	53.60

The method of analysis just described is not applicable to those nitro compounds in which the nitro group is attached to a tertiary carbon atom. The only compound of this type investigated was 2-nitro-*iso*butane. Mixtures of this compound with *tert.*-butyl nitrite were analyzed in two ways. The amount of the ester present was determined by hydrolyzing the mixture in the presence of standard acid and also by saponifying in

a standard solution of sodium hydroxide. The average of three determinations by each method agreed to within less than a tenth of a per cent. The percentage of nitro compound was calculated by difference.

A summary of the data obtained in this investigation of the iodides and bromides is given in Tables III and IV. The name of the alkyl halide undergoing reaction with silver nitrite is given in Col. 1 of Table III, the boiling range of the alkyl halide in Col. 2 and the weight of alkyl halide used in each preparation in Col. 3. The weight of silver nitrite used is given in Col. 4. In Col. 5 are given the boiling-point ranges of the mixture of isomers. The weights of the mixture of isomers are given in Col. 6 for each of two preparations. The percentages of nitrogen found by Dumas determinations in the mixture of isomers are given in Cols. 7 and 8. The percentages of nitrogen theoretically present in the nitrite and nitro compound concerned are given in Col. 9.

TABLE III

DATA FOR VARIOUS PREPARATIONS OF MIXTURES OF ALKYL NITRITES AND NITROPARAFFINS

Alkyl halide			$AgNO_2$,	Yield			
Name	B. p., °C.	G.	g.	B. p., °C.	G.	N, found, %	Calcd., %
n-Propyl	102–102.5	50	60 + 15	56–132	22.0	16.16	16.6	15.70
iodide	102–102.5	50	60 + 15	56–132	23.5	15.55	15.41	15.70
Sec.-propyl	89–89.5	50	60 + 15	44–120	19.0	15.30	15.35	15.70
iodide	89–89.5	50	60 + 15	44–120	18.6	15.15	...	15.70
n-Butyl	126.5–127	50	50 + 15	74–152	23.8	13.92	13.45	13.59
iodide	126.5–127	50	50 + 15	74–152	24.5	13.37	13.15	13.59
*Iso*butyl	120–120.5	50	50 + 15	66–139	21.2	13.25	13.35	13.59
iodide	120–120.5	50	50 + 15	66–139	20.8	13.40	13.32	13.59
Sec.-butyl	116.2–117.3	50	50 + 15	67–140	19.8	13.22	13.42	13.59
iodide	116.2–117.3	50	50 + 15	67–140	19.5	13.52	...	13.59
n-Propyl	69.5–71	40	50 + 15	56–132	24.8	15.62	...	15.70
bromide	69.5–71	40	50 + 15	56–132	25.3	15.45	...	15.70
Sec.-propyl	58–59.2	40	50 + 15	44–120	23.0	15.15	15.50	15.70
bromide	58–59.2	40	50 + 15	44–120	22.6	15.46	15.15	15.70
n-Butyl	100–102	50	60 + 15	74–152	33.3	13.65	13.40	13.59
bromide	100–102	50	60 + 15	74–152	32.9	13.65	...	13.59
*Iso*butyl	89.5–91	50	60 + 15	66–139	29.3	13.35	13.38	13.59
bromide	89.5–91	50	60 + 15	66–139	28.7	13.25	...	13.59
Sec.-butyl	90–91.2	45	55 + 15	67–140	23.2	13.25	13.48	13.59
bromide	90–91.2	45	55 + 15	67–140	23.0	13.15	...	13.59
Tert.-butyl	72–73.1	50	60 + 15	62–127	22.5	13.15	...	13.59
bromide	72–73.1	50	60 + 15	62–127	...	...	...	...
Iso-amyl	120–121	50	55 + 15	98–160	30.0	11.75	...	11.95
bromide	120–121	50	55 + 15	98–160	30.4	11.65	...	11.95
n-Heptyl	177–178.5	50	50 + 15	154–196	38.5	9.54	9.57	9.64
bromide	177–178.5	50	50 + 15	154–196	38.0	9.47	...	9.64
Sec.-octyl	71 (14 mm.)	50	45 + 15	164–213	35.5	8.51	8.40	8.80
bromide	71 (14 mm.)	50	45 + 15	164–213	34.2	8.58	8.45	8.80
Allyl	69–71	25	35 + 10	43–130	15.2	15.85	...	16.08
bromide	69–71	21.5	30 + 10	43–130	13.2	15.70	...	16.08

TABLE IV

YIELDS OF NITROPARAFFIN AND ALKYL NITRITES

Alkyl radical	Iodides		Bromides	
	Mixed isomers isolated, %	Nitro compound in mixture, %	Mixed isomers isolated, %	Nitro compound in mixture, %
Allyl	..	..	74.0	79.8
n-Propyl	85.9	66.9	86.1	77.4
Sec.-propyl	71.7	31.8	78.5	40.3
n-Butyl	85.1	60.7	88.2	77.9
*Iso*butyl	74.9	40.0	77.2	57.8
Sec.-Butyl	70.0	31.9	68.3	30.0
Tert.-butyl	..	..	60.0	48.3
Iso-amyl	..	..	78.2	67.5
n-Heptyl	..	..	94.3	71.0
Sec.-octyl	..	..	82.1	34.3

From three to five combustions were carried out on samples of each of the two preparations for each of the alkyl halides. Combustions on the same preparation never varied more than 1.7% from the average and in the great majority of cases the variation was not more than 0.5%. Combustions on different preparations never varied more than 1.1% from the average and rarely more than 0.7%. The averages of all these data are given in Table IV along with the average (two or more preparations) yield of mixed isomers.

n-Butyl chloride apparently does not react at its boiling point with silver nitrite as do the bromide and iodide. *Iso*-amyl chloride reacted but not at all completely when it was refluxed with silver nitrite. When 25 g. was heated with 45 g. of silver nitrite in a sealed tube at the boiling point of toluene for twenty-four hours, the product, weighing 22 g., contained 10.1% of chlorine calculated as *iso*-amyl chloride. The percentage of nitrogen in a mixture of the isomers with this percentage of the alkyl halide would be 10.77%. Actually 10.47 and 10.62% of nitrogen was found by analysis by the Dumas method. The analysis of the mixture showed that the isomers were present in the ratio of 30.1% of the nitro-*iso*pentane to 69.9% of the *iso*-amyl nitrite. The yield of the mixture of isomers was calculated to be 81.1% of the theoretical after allowance had been made for the unreacted *iso*-amyl chloride. Attempts to secure complete reaction of the *iso*-amyl chloride were unsuccessful.

Discussion of Results

The experimental results may be considered from several points of view.

I. A Comparison of Alkyl Iodides and Bromides as to the Amounts and the Proportions of Nitro Compound and Nitrite Formed.—A larger percentage of nitro compound was produced from the alkyl bromides than from the alkyl iodides, except in the case of *sec.*-butyl bromide. The percentage of 2-nitrobutane formed from *sec.*-butyl bromide was 1.3% less than that formed from *sec.*-butyl iodide.

The yields of mixtures isolated were from 10 to 17% higher with the bromides than with the iodides, except in the case of *sec.*-butyl bromide. *Sec.*-butyl iodide gave 1.7% higher yields than did *sec.*-butyl bromide.

II. The Relation of the Branching of the Chain as to the Proportion of the Isomers Formed.—The primary halides containing a branched chain did not give as high a proportion of nitro compound as did the straight chain compounds. For example, *iso*butyl bromide gave 57.9% of the nitro compound while *n*-butyl bromide gave 77.9% of nitro compound. The effect of the *iso* grouping in lowering the proportion of nitro compound apparently becomes less pronounced as it is further removed from the halogen. *Iso*pentyl bromide gave 67.5% of the nitro compound, a proportion which approaches, although it is distinctly lower than, that for a straight chain bromide.

III. The Relation of the Position of the Halogen to the Proportion of the Isomers Found.—If the halogen in the alkyl halide is on a *sec.*-carbon atom, the proportion of nitro compounds is materially less than it is for the corresponding primary alkyl halide. In the case of the propyl and butyl compounds the proportion of the nitro compounds from the *sec.*-halides is in the vicinity of one-half the percentages in the case of the primary halides. It was rather surprising to find that with a branched chain and with the halogen on a *tert.*-carbon atom the proportion of nitro compound was higher than it was for the corresponding *sec.*-halide. *Tert.*-butyl bromide showed 48.3% of nitro compound as contrasted with 30% for the *sec.*-butyl and 57.9% for the *iso*butyl. Sidgwick states that tertiary halides gave almost entirely the nitrite and very little of the nitro compound. Tscherniak found that by the interaction of *tert.*-butyl iodide and silver nitrite, very little 2-nitro-*iso*butane was formed, but a larger percentage of the *tert.*-butyl nitrite was formed, no figures being reported.

IV. The Effect of Lengthening the Chain as to Proportion of the Isomers Formed.—It cannot be stated that there was in general either an increase or a decrease in proportions of nitro compound with increasing molecular weight of the alkyl group. *n*-Butyl iodide gave 5% lower than *n*-propyl iodide while *n*-butyl bromide gave 0.5% higher than the *n*-propyl bromide. *n*-Heptyl bromide gave only 6% less than the butyl compound. In the case of the iodides there was no difference between *sec.*-propyl and *sec.*-butyl, while in the case of bromides the percentage of nitro compounds dropped from 40.3 to 30%. Going higher in the secondary series to *sec.*-octyl, there is a slight increase in the proportion of nitro compound. As has been noted above in the case of the *iso*-compounds, there was a considerable increase in the proportion of nitro compound with increasing molecular weight. Sidgwick[9] states that all halides con-

[9] Sidgwick, "The Organic Chemistry of Nitrogen," The Clarendon Press, Oxford, 1910, p. 140.

taining more than 4 carbon atoms give very low yields of the nitro compound.

V. The Effect of Unsaturation as to Proportion of the Isomers Formed.—The porportion of nitro compound formed from allyl bromide as compared with that of *n*-propyl bromide indicates that unsaturation has little or no effect on the relative proportions of nitro compound and alkyl nitrite formed.

VI. Relation between Constitution of the Alkyl Halide and Yield of the Mixture of Isomers.—The highest yields of the mixed isomers were isolated from the reaction of normal alkyl halides, the yield increasing with lengthening of chain in the case of alkyl bromides. *n*-Butyl iodide gave an 0.8% lower yield than did *n*-propyl iodide. With the exception of the *sec.*-butyl halides, the *sec.*-alkyl halides gave better yields than did the *iso*-alkyl halides. *Sec.*-butyl iodide gave a 70% yield and the corresponding bromide a 68.3% yield, while *sec.*-octyl bromide gave an 82% yield. *Sec.*-propyl iodide and *iso*butyl bromide gave an 82% yield. *Sec.*-propyl iodide and *iso*butyl iodide gave 71.8 and 74.9% yields, respectively, while the corresponding bromides gave 78.5 and 77.3% yields, respectively. Allyl bromide gave a yield of 74%. A yield of only 60% was obtained from *tert.*-butyl bromide.

VII. Relation between Constitution of Alkyl Halides and Rapidity of Reaction.—The reaction was more rapid with the branched chain alkyl halides and with the secondary halides than it was with the straight chain, normal alkyl halides. *Tert.*-butyl bromide was the most active of all the saturated alkyl bromides used. The secondary alkyl bromides were more active than the corresponding *iso*-alkyl halides. Allyl bromide was the most active of all the bromides used. The alkyl iodides react much more rapidly than do alkyl bromides, but the relative reactivities of the various iodides were about the same as with the bromides.

VIII. A Comparison of iso-Amyl Chloride and Bromide.—The proportion of nitro compound was much less in the case of the reaction of *iso*-amyl chloride than it was for *iso*-amyl bromide. The chloride reacts less rapidly but the yield of the mixture of isomers is about the same as for the bromide.

IX. Mechanism of Reaction.—There seems to have been no adequate hypothesis advanced to account for the differences in the ratio of alkyl nitrites and nitroparaffin produced by the reaction of different alkyl iodides.[10] (Apparently it has not been previously realized that the nature of the halogen also played an important role in determining the proportion of the

[10] (a) E. Reynolds, *J. Chem. Soc.*, **83**, 643 (1903); (b) Ray and Ganguli, *Proc. Chem. Soc.*, **21**, 278 (1905); (c) Diners, *ibid.*, **21**, 281 (1905); (d) Ray and Neogi, *J. Chem. Soc.*, **89**, 1905 (1906); (e) Neogi, *ibid.*, **105**, 2371 (1914); (f) Neogi and Chowdhuri, *ibid.*, **109**, 701 (1916).

isomers formed.) It seems probable to the authors that the two reactants form an addition compound, as suggested by Nef for the cyanides and isocyanides, although it may well be questioned whether a molecular compound is not formed instead of definite primary valences being set up as postulated by Nef. Each component of this molecular compound, alkyl group, metal and halogen, would then exert its influence in determining the relative rates of the two modes of decomposition whereby nitroparaffin and alkyl nitrite are formed.[11] This hypothesis is vague; it explains nothing and predicts nothing, yet it seems that at least for the present it is not possible to advance a more specific one without going far beyond experimental justification.

Summary

A quantitative study has been made of the amount and proportion of isomeric nitroparaffins and alkyl nitrites simultaneously formed through the reaction of silver nitrite and the following list of alkyl halides: *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl and *sec.*-butyl iodides, and *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, *sec.*-butyl, *tert.*-butyl, *iso*-amyl, *n*-heptyl, *sec.*-octyl and allyl bromides and *iso*-amyl chloride.

It was found that a larger proportion of nitro compound was produced from the bromides than from the iodides except in the case of *sec.*-butyl bromide. *Iso*-amyl bromide gave over twice as large a percentage of the nitro compound as did the *iso*-amyl chloride. The yield of the isomers isolated was from 10 to 17% higher from the bromides than from the iodides, except in the case of *sec.*-butyl bromide. Primary halides containing a branched chain did not give as high a proportion of nitro compound as did the straight chain compounds. If the halogen in the alkyl halide is on a secondary carbon atom, the amount of formation of the nitro compound is materially less than it is for the corresponding primary or tertiary alkyl halide. It cannot be said that there is in general either an increase or a decrease in proportion of nitro compounds with increasing molecular weight of the alkyl group. The results obtained with allyl bromide indicate that unsaturation has little or no effect on the ratio of isomers formed. The highest yields of the mixed isomers were isolated from the reaction of normal alkyl halides, the yield increasing with lengthening of the chain in the case of the bromides. The order of increasing reactivity of the alkyl halides is allyl, *tert.*-butyl, *sec.*-halides, *iso*-alkyl, and *n*-alkyls. The iodides are more reactive than the bromides.

Attempts to prepare mixtures of the isomers sufficiently pure for analysis were unsuccessful when *tert.*-butyl iodide, cyclohexyl iodide, benzyl bromide or 2-phenylethyl bromide was used.

MADISON, WISCONSIN

[11] *Cf.* Falk, "Chemical Reactions, Their Theory and Mechanism," Chemical Catalog Co., New York, 1920.