Space does not allow a careful marshaling of cases of clear primary valence and clear secondary valence and of cases like this one of nickel carbonyl which has some characteristics of both kinds of valence. Suffice it to say, that using the term in the vague sense that describes only the general nature of the substance and not its precise structure, nickel carbonyl is properly classified as a secondary valence compound. The only way in which valence may be precisely defined is by stating the kernel charge, the number of electrons in the sheath and the number held in common with other atoms. When this is guesswork, the valence itself is guesswork. Guesses of this kind are justifiable when they lead ultimately to a satisfactory system of classification.

Summary

Experimental data concerning the reaction of nickel carbonyl with the non-metals bromine, sulfur, oxygen and with the Grignard reagent are given.

The data support the claim that nickel carbonyl is a compound in which secondary valence alone is exerted, either constituent being free to enter into its ordinary reactions, the other constituent being thereby left alone in its ordinary free condition.

A structure of the extremely volatile carbonyls is proposed which would give a very small stray electrostatic field; the sheath of the metal atom contains 18 electrons in each case.

An interesting case of the formation of formic acid in small amount from carbon monoxide and water during the slow oxidation of nickel carbonyl is incidentally brought to light.

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VELOCITY—TEMPERATURE COEFFICIENT IN LIQUID MEDIA

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The measurements to be found in the literature on the velocity of strictly homogeneous, isolated reactions both in the gaseous state and in liquid media, show in the majority of cases that the effect of temperature is given within the experimental error of the measurements by the relation, $d\, ln\, k/dT = E/RT^2$, in which E is a constant characteristic of the reaction and the medium.

This is the relation originally proposed by Arrhenius and shown by him to be a consequence of his theory of the active-passive molecule equilibrium and of other postulates so improbable that the equation has until recent years been considered empirical. However, in the recent intensive application of the kinetic theory, the distribution law and the quantum hypothesis to the problem of reaction velocity,[1] an equation of the Arrhenius form has been developed for gaseous reactions on the basis of somewhat different assumptions and different modes of attack. In these more recent developments of the equation, E obtains a physical significance, for example, the difference between the energy per mole of the molecules which enter into reaction and the mean energy per mole of the reactants. E, according to some of these treatments, is a constant independent of temperature; according to others, it should vary slightly with temperature.

Trautz alone has from the theoretical side comprehensively considered the more complicated problem of reaction velocity in solution. His conclusions will be briefly discussed in connection with the interpretation of the results of our measurements.

The object of these experiments was the very accurate determination of the velocity-temperature coefficients of a number of reactions in each of several organic solvents in order to determine to what extent this often apparent constancy of E is a fact and by means of such a series of measurements to separate, in so far as possible, the effect of the change in the medium with change in temperature upon E, from the pure temperature coefficient of E. The few isolated velocity measurements of high accuracy available in the literature[2] are over too small a temperature range or insufficiently related to permit separation of the medium effect from the temperature effect.

In this work the velocity and temperature coefficients have been determined over a considerable range of temperature for the reactions, $C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$, in nitrobenzene, acetylene tetrachloride and benzyl alcohol; $C_5H_5N + CH_3I = C_5H_5NCH_3I$ in acetylene tetrachloride (reactions not heretofore studied) and the decomposition of triethylsulfine bromide, $(C_2H_5)_3SBr$, in nitrobenzene and acetylene tetrachloride.[3]

Reagents

Solvents.—Nitrobenzene, from the Eastman Kodak Company, was washed, dried with calcium chloride and distilled. It distilled completely within a range of 0.5°.

Acetylene tetrachloride, from the Will Corporation, marked C. P., was washed, dried with calcium chloride and distilled.

Benzyl alcohol, from Eimer and Amend, marked C. P., was dried with anhydrous sodium sulfate and distilled. The portion used had a boiling-point range of 0.5°.

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[1] Marcelin, *Ann. Phys.*, **3,** 120 (1915). Rice, *Brit. Assoc. Advancement Sci. Repts.*, **1915,** p. 397. Lewis, *J. Chem. Soc.*, **113,** 471 (1918). Trautz, *Z. anorg. chem.*, **102,** 81 (1918). Tolman, THIS JOURNAL, **42,** 2506 (1920).

[2] See particularly the work of Rice and Kilpatrick, THIS JOURNAL, **45,** 1401 (1923).

[3] Compare von Halban, *Z. physik. Chem.*, **67,** 129 (1909).

Reactants.—Especial care was taken in the purification of the reactants.

Dimethyl aniline, from the Eastman Kodak Company, marked "free from monomethylaniline," was washed, dried with potassium hydroxide and distilled. The boiling-point range was 0.1°.

Methyl iodide, from the same source, was washed, kept for one month over calcium chloride and distilled. The portion used had a boiling-point range of 0.2°. It was water-white, was kept in a dark bottle and the remainder showed no trace of color after two years and the completion of the experiments. A portion of the methyl iodide was allowed to react for one month with an excess of dimethylaniline in nitrobenzene. Analysis of the salt formed showed a methyl iodide content of 99.32%, indicating a purity of the reagent in excess of this value.

Pyridine, from the same source, was purified by the recently published method of Heap, Jones and Speakman.[4] The boiling point was constant.

Triethylsulfine bromide was prepared from ethyl sulfide and ethyl bromide by the method of von Halban.[3] It was purified by repeated precipitation from alcoholic solution with ether and kept for several days in a vacuum over sulfuric acid to remove the last traces of solvent. This procedure had previously been shown to result in a practically pure product.

Experimental Part

In view of the problem, especial care was taken to make the velocity measurements on the different reactions in the same solvent and on each reaction at different temperatures, strictly comparative. To insure identity in solvents and reactants, a sufficient amount of each was purified at one time for the entire series of experiments in which it was to be used, and each was kept in a single stoppered bottle and in the dark wherever a light effect might be anticipated. To insure complete comparability between the *k* values for each reaction in a solvent at different temperatures, the initial concentrations were the same and the reaction was allowed to go at each temperature to the same point of fractional completion and not sufficiently far to admit more than a minimum of interference from the reverse reaction. In order to ascertain the proper time for the removal of the sample, preliminary rough measurements of the velocity were made at the various temperatures. In the single case, $C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$ in nitrobenzene, in which the velocity of the reverse reaction was of sufficient magnitude to require consideration, the equilibrium constant was determined and used in the calculations.

In the comparative experiments for each reaction at different temperatures, all details of the runs were made as nearly identical as possible; for example, in the extraction of the reaction product from the solvent, each

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[4] Heap, Jones and Speakman, THIS JOURNAL, **43**, 1936 (1921).

sample was extracted the same number of times, each extraction was made with the same volume of water and was shaken for the same period of time.

Duplicate experiments were run in every case. The average deviation from the mean of the *k* values in duplicates were: for $C_6H_5N(CH_3)_2$ + CH_3I in benzyl alcohol, 0.17%, in nitrobenzene, 0.07%; in acetylene tetrachloride, 0.17%; for C_5H_5N + CH_3I in acetylene tetrachloride, 0.16%; for the triethylsulfine bromide decomposition in nitrobenzene, 0.38%, in acetylene tetrachloride, 0.19%. These values indicate the magnitude of the errors due to analysis and time. Temperatures were read with a Leeds and Northrup potential terminal resistance thermometer, calibrated by the Bureau of Standards. The errors due to inconstancy or inaccuracy in the measurement of temperature are inappreciable in comparison with the errors due to time and analysis.

The concentrations used in the calculation of the velocity constants are the concentrations at the temperature of the experiment; for the cases for which data were not available in the literature for the calculations, the thermal expansion of the solvent was determined over the temperature range of the measurements.

The exigencies of the several reactions required somewhat different experimental procedures. The procedures briefly outlined below are those finally adopted, often after several methods which had proven unsatisfactory had been discarded.

Dimethylaniline and Methyl Iodide in Nitrobenzene.—One hundred and ninety-five cc. of nitrobenzene was placed in a 200cc. Pyrex flask, the neck of which passed through a rubber stopper, and the flask and solvent were weighed accurately to four places. One cc. of methyl iodide was added, the flask stoppered, shaken, weighed again and placed in the constant-temperature bath. After the reaction vessel had reached the temperature of the bath, a 2cc. pipet-full of dimethylaniline was added, the time noted, the reaction flask stoppered, shaken and completely immersed in the constant-temperature bath. The weight of dimethylaniline added was determined by weighing the pipet and a flask containing dimethylaniline, before and after the withdrawal of the sample. The pipet fitted into the flask containing the dimethylaniline through a rubber stopper which prevented possible error due to volatility or moisture absorption. When the reaction had proceeded to the desired extent, the reaction flask was removed from the bath, inverted into a wide-mouth bottle containing dil. nitric acid, into the neck of which fitted the rubber stopper around the neck of the reaction flask; the time was noted and the vessels were shaken to stop the reaction completely. The mixture was then transferred to a 1-liter separatory funnel, 450 cc. of benzene added to float the nitrobenzene and the mixture shaken vigorously for one minute. The water layer was drawn off through a wet filter to catch droplets of oil. The oil layer was extracted twice more, each time with 200 cc. of cold water, the filtrates were combined and the quantity of salt was determined gravimetrically as silver iodide.

In the preliminary measurements, the standard gravimetric procedure was followed in the determination of iodine as silver iodide, the precipitate being boiled with a slight excess of the silver nitrate. It was discovered, however, that sufficient methyl iodide was extracted by the water and reacted at boiling temperature to form silver iodide, to introduce an error in the calculated velocity constant of about 2%. Investigation showed that the iodine in the salt could be determined accurately without heating and without interference due to the presence of the slight amount of methyl iodide in the water solution. This was the procedure followed in the final measurements.

The possibility that the temperature inside the reaction vessel might be appreciably different, due to heat of reaction, from that of the bath in which the temperature was read, was considered and eliminated by separate experiments with resistance thermometers inside and out; but this is a possible source of error which should always be considered and may not be negligible. It was found necessary, for instance, to take account of this heat effect in the triethylsulfine bromide reaction in acetylene tetrachloride at the higher temperatures where the velocity is greatest.

A small drop in the "constant" with time in the orientation measurements showed, however, in this case, that when the reaction had been allowed to become one-third complete, the reverse reaction caused a small but not negligible disturbance. The equilibrium constant was, therefore, determined and the velocity constant of the isolated direct reaction calculated. For bimolecular addition the differential equation is $dx/dt = k_1(a-x)(b-x)-k_2x$, or $dx/k_1dt = (a-x)(b-x)-Kx$, which integrated gives

$$k_1 = \frac{1}{t\sqrt{(a-b)^2+K(K+2a+2b)}} \ ln \frac{2ab - x[(a+b+K) - \sqrt{(a-b)^2+K(K+2a+2b)}]}{2ab - x[(a+b+K) + \sqrt{(a-b)^2+K(K+2a+2b)}]}$$

the equation used in our final calculation.

The magnitude of the effect of the reverse reaction at different temperatures is shown in Table I. The determined values of the equilibrium constant were $K_{60.7°} = 0.0156$ and $K_{50.4°} = 0.00757$. K values at the other temperatures were calculated from the reaction isochor.

The determined values of the equilibrium constant may be considerably in error but great accuracy was not necessary for this purpose as K entered into the calculation only as a small correction factor. The effect of the correction on the relative values of $E_{\text{obs.}}$ is small.

Dimethylaniline and Methyl Iodide in Benzyl Alcohol.—The procedure

Table I

$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$ in Nitrobenzene

Effect of Reverse Reaction

Temp., °C.	K	k, reverse reaction not considered, av.	k_1, using K and modified formula, av.	$E_{obs.}$ from k	$E_{obs.}$ from k_1
10.11	0.00031	0.001722	0.001724		
				12943	12959
20.03	.00068	.003748	.003756		
				12540	12578
30.03	.00160	.007621	.007654		
				13183	13287
39.95	.00357	.01524	.01539		
				12837	13056
50.02	.00754	.02898	.02960		
(*a*) 10.11	.00031	.001725	.001727		
				12890	12903
(*a*) 19.95	.00068	.003720	.003727		

(*a*) Repetitions.

was essentially that described for the same reaction in nitrobenzene, the only modification being one additional water extraction necessitated by the greater solubility of the salt in this solvent. The orientation experiments showed no disturbance from the reverse reaction. The heat of reaction effect was not determined but estimations, based on the heat of the reaction (roughly determined in this Laboratory), the surface of the reaction vessel and the velocity of the reaction, indicate that the effect is negligible in comparison with the other experimental errors even at the highest temperatures.

Dimethylaniline and Methyl Iodide in Acetylene Tetrachloride.—The same procedure was followed in the study of this reaction in acetylene tetrachloride as in benzyl alcohol with the exception that in this case no attempt was made to float the heavy acetylene tetrachloride solution. The reverse reaction did not interfere to an appreciable extent. The heat of reaction effect was considered negligible.

Pyridine and Methyl Iodide in Acetylene Tetrachloride.—The procedure was identical with that described for the reaction in the same solvent described in the preceding paragraph. The reverse reaction did not interfere. The effect of heat of reaction was considered negligible.

Decomposition of Triethylsulfine Bromide in Nitrobenzene.—Enough of a saturated solution of the compound in nitrobenzene was prepared to last for a complete series of runs. To prevent appreciable decomposition of the salt the solution was kept below 10° until the end of the series of experiments.

For a run at the highest temperature, 850 cc. of the solution was placed in a long-neck 1-liter flask, brought rapidly to approximately the temperature at which the run was to be made and then all but 5 cm. of the neck of the flask submerged in the constant-temperature bath. It was allowed to remain there for one-half hour and frequently shaken, before the initial sample was taken. At the lower temperatures the initial samples were not withdrawn until the reaction had proceeded to about the same extent as at the highest temperature, the required time being calculated from preliminary runs.

Two initial samples of 200 cc. each were withdrawn, using 200cc. pipets which before use were kept in tubes immersed in the constant-temperature bath. Each sample, immediately after withdrawal, was allowed to run into distilled water at 0°, the time noted, and the salt extracted by shaking with this and two additional portions of cold water. The water solutions were combined, filtered through wet filter paper and the salt was determined gravimetrically as silver bromide. Final samples were removed, treated and analyzed in the same manner.

At all temperatures, initial and final samples were removed at roughly the same fractional completion. No corrections were made for changes in temperature due to the heat of the reaction, and consideration of the extreme dilution of the solutions and the data obtained on the effect of the heat of the same reaction in acetylene tetrachloride indicated that no correction was necessary. The extreme dilutions necessary, due to the slight solubility of the salt in nitrobenzene, make these determinations the most inaccurate of the series.

Decomposition of Triethylsulfine Bromide in Acetylene Tetrachloride.—The method used in following this reaction was, with the exception of the details noted below, that of the same reaction in nitrobenzene. An improved method of withdrawing the samples was used, the stopper of the reaction flask being fitted with a glass tube reaching to the bottom of the flask. When it was desired to withdraw a sample, connection was made with a bottle containing the cold water and the sample rapidly pulled over by suction. The amount of sample was determined by weighing the receiving bottle before and after collection of the sample. This method of withdrawal proved to be a considerable improvement. The transfer being more rapid, the time measurement was more accurate. The gravimetric determination of quantity of sample is more accurate than the volumetric. Since it was unnecessary either to remove the stopper of the reaction vessel or insert a sampling tube, sampling created a minimum of disturbance in the temperature of the reaction mixture. During the run, at the higher temperatures, the reaction flask was shaken at ten-minute intervals.

The heat of this reaction appreciably influenced the temperature of the reaction mixture at the higher temperatures. The correction necessary was determined by independent runs at 60° and 50°, with resistance thermometers inside and outside. The reaction is endothermic. At 60°, the temperature inside averaged 0.17° lower, at 50°, 0.03° lower than the temperature of the bath. From these values the much smaller differences were calculated for the lower temperatures.

Results

The data and results are presented in Tables II, III, IV, V, VI and VII and the $E_{\text{obs.}}$ values collected for comparison in Table VIII.

TABLE II

$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$ IN NITROBENZENE

Initial concentrations: dimethylaniline, 0.075 M (±3%); methyl iodide, 0.086 M (±3%). Reaction allowed to go to 0.3 (±5%) completion.

Temp., °C.	10.11		20.03		30.03		39.95		50.02	10.11[a]		19.95[a]
$k \times 10^4$	17.24		37.56		76.54		153.9		296.0	17.27		37.27
$E_{\text{obs.}}$		12959		12578		13287		13056			12903	

[a] Repetitions

TABLE III

$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$ IN BENZYL ALCOHOL

Initial concentrations: dimethylaniline, 0.153 M (±3%); methyl iodide, 0.175 M (±3%). Reaction allowed to go to 0.45 (±5%) completion.

Temp., °C.	10.11		20.03		30.02		39.95		50.02	10.11[a]		19.95[a]
$k \times 10^4$	21.16		50.24		114.5		241.8		499.3	21.16		49.87
$E_{\text{obs.}}$		14390		14565		14220		14472			14378	

[a] Repetitions

TABLE IV

$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$ IN ACETYLENE TETRACHLORIDE

Initial concentrations: dimethylaniline, 0.151 M (±3%); methyl iodide, 0.173 M (±3%). Reaction allowed to go to 0.33 (±5%) completion.

Temp., °C.	19.92		29.87		39.94		49.98
$k \times 10^4$	29.78		58.15		108.7		192.8
$E_{\text{obs.}}$		11873		11689		11479	

TABLE V

$C_5H_5N + CH_3I = C_5H_5NCH_3I$ IN ACETYLENE TETRACHLORIDE

Initial concentrations: pyridine, 0.228 M (±3%); methyl iodide, 0.172 M (±3%). Reaction allowed to go to 0.66 (±5%) completion.

Temp., °C.	19.92		29.87		39.94		49.98
$k \times 10^4$	71.29		150.2		305.4		588.9
$E_{\text{obs.}}$		13230		13278		13153	

TABLE VI

$(C_2H_5)_3SBr = (C_2H_5)_2S + C_2H_5Br$ IN NITROBENZENE

Initial concentration of $(C_2H_5)_3SBr$, 0.015 M to 0.010 M; final concentration, 0.007 M to 0.0046 M.

Temp., °C.	20.01		29.96		40.29		50.12		60.01
$k \times 10^4$	0.2706		1.398		7.454		29.30		105.2
$E_{\text{obs.}}$		29152		30600		28049		27672	

TABLE VII

$(C_2H_5)_3SBr = (C_2H_5)_2S + C_2H_5Br$ IN ACETYLENE TETRACHLORIDE

Initial concentration of $(C_2H_5)_3SBr$, 0.037 *M* to 0.028 *M;* final concentration, 0.021 *M* to 0.010 *M*.

Temp., °C.	20.08		29.85		39.91		50.01		59.79
$k \times 10^4$	0.2943		1.588		7.978		36.88		155.2
$E_{obs.}$		30472		30257		30485		31428	

TABLE VIII

SUMMARY, VALUES OF $E_{obs.}$

Temp., °C.	15	25	35	45	55
SOLVENT: NITROBENZENE					
$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$					
	12,959	12,578	13,287	13,056	
$(C_2H_5)_3SBr = (C_2H_5)_2S + C_2H_5Br$					
		29,152	30,600	28,049	27,672
SOLVENT: ACETYLENE TETRACHLORIDE					
$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$					
		11,873	11,689	11,479	
$C_5H_5N + CH_3I = C_5H_5NCH_3I$					
		13,230	13,278	13,153	
$(C_2H_5)_3SBr = (C_2H_5)_2S + C_2H_5Br$					
		30,472	30,257	30,485	31,428
SOLVENT: BENZYL ALCOHOL					
$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$					
	14,390	14,565	14,220	14,472	

These $E_{obs.}$ values are calculated from the equation $d\ ln\ k/dT = E/RT^2$ and are referred to in the text with the subscript. E values calculated from the formula $(d\ ln\ (k/\sqrt{T})/dT) = E/RT^2$, to be discussed, parallel the values tabulated and are a few hundred calories lower.

For the reactions in acetylene tetrachloride, for the range 25° to 45°, $E_{obs.}$ is practically independent of temperature, the deviations from constancy for the reaction between pyridine and methyl iodide and the decomposition of triethylsulfine bromide being well within the experimental errors of the measurements; for the reaction between dimethylaniline and methyl iodide, $E_{obs.}$ decreases slightly with temperature. The decomposition of triethylsulfine bromide, the only reaction for which E was obtained at a higher temperature in this solvent, shows a markedly higher value of $E_{obs.}$ at 55°.

For the reaction between dimethylaniline and methyl iodide in benzyl alcohol, $E_{obs.}$ is independent of temperature over the entire range of the measurements.

In nitrobenzene, both of the reactions exhibit a maximum in $E_{\text{obs.}}$ at 35°. A maximum at this temperature is also apparent in every one of several preliminary runs with each of these reactions in this solvent, so that a maximum in $E_{\text{obs.}}$ at 35° may be considered as established, for these two reactions in this solvent. The determined values of k and $E_{\text{obs.}}$ for the decomposition of triethylsulfine bromide in nitrobenzene, due to the necessarily extreme dilution of the solutions, are considerably the most inaccurate of the series.

The downward trend in $E_{\text{obs.}}$ with increase in temperature, noticeable in the decomposition reaction in nitrobenzene and apparent to a less extent in the reaction between dimethylaniline and methyl iodide in acetylene tetrachloride, may be due to the occurrence of a simultaneous reaction to a slight extent. The observed maxima in $E_{\text{obs.}}$, particularly in view of the fact that they occur at the same temperature for different reactions in the same solvent, are not satisfactorily explained by such an assumption.

Simultaneous reactions, other than the opposing reaction of which account was taken when necessary, as described, were not detected in the orientation experiments.

Theoretical

For bimolecular reactions in gases it follows from the distribution law and the collision frequency relation of the kinetic theory as shown by Trautz[5] and others that

$$k = \mathrm{N}\,\sigma^2 \sqrt{8\,\pi\,RT\,\frac{M_\mathrm{A}+M_\mathrm{B}}{M_\mathrm{A}\cdot M_\mathrm{B}}}\cdot e^{\int \frac{q_\mathrm{A}+q_\mathrm{B}}{RT^2}\cdot \mathrm{d}T}$$

in which N is the Avogadro constant, σ the average molecular diameter of A and B, M_A and M_B are their molecular weights and q_A and q_B the energies of activation. The validity of this relation has been tested by Dushman[6] who finds good agreement between the calculated and observed values of k.

Grouping together the factors independent of temperature, k = const. × $\sqrt{T}\cdot e^{\int \frac{q_\mathrm{A}+q_\mathrm{B}}{RT^2}\cdot \mathrm{d}T}$, which on differentiation gives $[\mathrm{d}\,ln(k/\sqrt{T})/\mathrm{d}T] = (q_\mathrm{A}+q_\mathrm{B})/RT^2$; $q_\mathrm{A}+q_\mathrm{B}$, the energy of activation, is the difference between the energy of the molecules per mole which enter into reaction and the mean energy per mole, $q_\mathrm{A}+q_\mathrm{B} = E = E_c - U$.

The manner of dependence of energy of activation (critical increment) on temperature will depend on the assumptions made regarding the temperature coefficient of E_c. If E_c (critical energy) is independent of temperature $[\mathrm{d}(q_\mathrm{A}+q_\mathrm{B})]/\mathrm{d}T = \mathrm{d}E/\mathrm{d}T = -\mathrm{d}U/\mathrm{d}T = -\Sigma C_{vi}$, in which ΣC_{vi} is the summation of the molal heat capacities of inactives.

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[5] Trautz, *Z. anorg. Chem.*, **102**, 86 (1918).

[6] Dushman, THIS JOURNAL, **43**, 397 (1921).

Then

$$E = E_{t=0} - \Sigma C_{vi} \cdot t; \quad \frac{\mathrm{d}\, ln \dfrac{k}{\sqrt{T}}}{\mathrm{d}T} = \frac{E_{t=0} - \Sigma C_{vi} \cdot t}{RT^2}$$

and E will decrease with temperature in the manner indicated. If on the other hand $\mathrm{d}E_c/\mathrm{d}T = \Sigma C_{va}$ (summation of molal heat capacities of actives) and $\Sigma C_{va} = \Sigma C_{vi}$, as postulated by Trautz, $[\mathrm{d}\, ln(k/\sqrt{T})]/dT = E_{t=0}/RT^2$ and E will be independent of temperature.

Turning now to bimolecular reactions in liquids, to which class belong also most apparently monomolecular reactions, Trautz,[7] who from the theoretical side has most thoroughly considered the modifications in the velocity-constant equation as derived from the distribution law and the collision frequency relation, consequent on the close packing of solute and solvent molecules, comes to the conclusion that the velocity constant of bimolecular reactions in solution should be given by

$$k = \text{const.}\ \sqrt{T} \cdot e^{\int \frac{q_A + q_B}{RT^2} \cdot \mathrm{d}T} . \phi T \tag{1}$$

ϕT includes the steric factor which takes account of the necessity that, for reaction, molecules collide at definite portions of their surfaces and of the influence of the solvent upon the duration of collisions and on the collision frequency. ϕT is always less than 1 and is not simply of the form $e^{-B/T}$.

The above relation on differentiation with regard to T gives

$$\frac{\mathrm{d}\, ln\ (k/\sqrt{T})}{\mathrm{d}T} = \frac{q_A + q_B}{RT^2} + \frac{\mathrm{d}\, ln\ \phi T}{\mathrm{d}T} \tag{2}$$

in which $q_A + q_B = E = E_c - U$.

If the critical energy is independent of temperature

$$\frac{\mathrm{d}\ (q_A + q_B)}{\mathrm{d}T} = \frac{\mathrm{d}E}{\mathrm{d}T} = -\frac{\mathrm{d}U}{\mathrm{d}T} = -\Sigma C_{vi}; \quad E = E_{t=0} - \Sigma C_{vi} \cdot t$$

and Equation 2 becomes

$$\frac{\mathrm{d}\, ln\ (k/\sqrt{T})}{\mathrm{d}T} = \frac{E_{t=0} - \Sigma C_{vi} \cdot t}{RT^2} + \frac{\mathrm{d}\, ln\ \phi T}{\mathrm{d}T} \tag{3}$$

If on the other hand E_c is a function of temperature and

$$\frac{\mathrm{d}E_c}{\mathrm{d}T} = \Sigma C_{va}$$

not greatly different from ΣC_{vi} as postulated by Trautz, then E = Const. $= E_{t=0}$

and

$$\frac{\mathrm{d}\, ln\ (k/\sqrt{T})}{\mathrm{d}T} = \frac{E_{t=0}}{RT^2} + \frac{\mathrm{d}\, ln\ \phi T}{\mathrm{d}T} \tag{4}$$

Accurate measurements of velocity-temperature coefficients on reactions between reactants of high molecular weight and covering several reactions in the same solvent should enable one to distinguish between the validity of Equations 3 and 4.

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[7] Trautz, *Z. anorg. Chem.*, **106**, 149 (1919).

Consider the measurements in acetylene tetrachloride for the range 25–45°. For the reaction, $C_6H_5N(CH_3)_2 + CH_3I$, from Kopp's Law for $C_6H_5N(CH_3)_2$, $C_v = 45.2$; for CH_3I, $C_v = 15.1$ and $\Sigma C_{vi} = 60.3$ or in solution $\Sigma C_{vi} > 60.3$. For the reaction $C_5H_5N + CH_3I$, $\Sigma C_{vi} > 42.9$ and for the $(C_2H_5)_3SBr$ decomposition, $\Sigma C_{vi} > 57.1$. For the first of these reactions if Equation 3 is correct, neglecting the $\mathrm{d}\,ln\,\phi T/\mathrm{d}T$ term the critical increment should decrease by 603 calories for 10° rise in temperature or 1206 calories for the range 25° to 45°. The observed decrease in E, calculated from the equation $\mathrm{d}\,ln\,(k/\sqrt{T})/\mathrm{d}T = E/RT^2$ or in our $E_{\text{obs.}}$ values which as previously remarked parallel the E values calculated from this equation, is much less than this and for the other reactions $E_{\text{obs.}}$ is certainly constant within the experimental errors. For any one reaction in this solvent the constancy of $E_{\text{obs.}}$ might be accounted for on the basis of Equation 3 by assuming that the increase in $ln\,\phi T$ with temperature had just counterbalanced the effect of the ΣC_{vi} term. The exact counterbalancing is improbable for any one reaction in this solvent; that these effects should counterbalance in each of several reactions in the same solvent is very improbable. On the other hand, the constancy of $E_{\text{obs.}}$ is in agreement with Equation 4 if we make the simple and plausible assumption that $\mathrm{d}\,ln\,\phi T/\mathrm{d}T$ is negligible within the experimental error of these measurements.

Each of the reactions in nitrobenzene exhibits a maximum in $E_{\text{obs.}}$ at 35°. This is best accounted for by the assumption of abnormality in ϕT which is predicted by the Trautz theory for reactions in solvents which are in other respects abnormal and at that temperature at which the other abnormalities occur.

For reactions in very abnormal solvents, the temperature coefficient of the velocity constant may show very considerable irregularity. Trautz and Volkmann[8] who measured the velocity of saponification of eight esters by alkalies in water from —10° to 70° found, without exception, a strongly accented maximum in the *k*-temperature coefficient at 25°. The authors in this case relate the irregularity to the coefficient of internal friction, a maximum in the temperature coefficient of which occurs at the indicated temperature.

Although irregularities in property-temperature curves are most marked in the liquids generally considered associated, they have been observed in liquids generally considered normal. Ethyl benzene and carbon tetrachloride show irregularities in their specific-heat–temperature curves at 40° and 35°, respectively. Williams and Daniels[9] consider this irregularity to be due to the heat of transition of one form of molecule to another. Williams and Daniels have also determined the specific-heat–temperature

[8] Trautz and Volkmann, *Z. physik. Chem.*, **64**, 53 (1908).

[9] Williams and Daniels, THIS JOURNAL, **46**, 903 (1924).

curve of nitrobenzene and in one of their two series of measurements, a distinct irregularity occurs at about 33°, corresponding excellently with the irregularity in our $E_{\mathrm{obs.}}$-temperature curves; in the other series the irregularity is not apparent.

Returning to a consideration of the reactions in acetylene tetrachloride, the $E_{\mathrm{obs.}}$ value for the decomposition of triethylsulfine bromide, which remains constant to 45° shows a considerably greater $E_{\mathrm{obs.}}$ value at 55°, which would appear to indicate an abnormality in acetylene tetrachloride at this temperature which should show itself by abnormally high $E_{\mathrm{obs.}}$ value with any reaction in this solvent, at this temperature.

Summary

1. Accurate determinations have been made of the velocity constant of the reactions (a) $C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$ in nitrobenzene at 10°, 20°, 30°, 40° and 50°; in acetylene tetrachloride at 20°, 30°, 40° and 50°; in benzyl alcohol at 10°, 20°, 30°, 40° and 50°; (b) $C_5H_5N + CH_3I = C_5H_5.CH_3NI$ in acetylene tetrachloride at 20°, 30°, 40° and 50°; (c) $(C_2H_5)_3SBr = (C_2H_5)_2S + C_2H_5Br$ in nitrobenzene and in acetylene tetrachloride at 20°, 30°, 40°, 50° and 60°. No previous velocity measurements have been made on the first two of these reactions.

2. Both reactions in nitrobenzene show a maximum in the $E_{\mathrm{obs.}}$ values at 35°.

3. $E_{\mathrm{obs.}}$ is apparently independent of temperature for the reaction $C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$ in benzyl alcohol.

4. For each of the three reactions in acetylene tetrachloride, the $E_{\mathrm{obs.}}$ value is practically independent of temperature over the range 25° to 45°. The $E_{\mathrm{obs.}}$ values for this range are constant, well within the experimental errors for the reactions $C_5H_5N + CH_3I = C_5H_5.CH_3NI$, and $(C_2H_5)_3SBr = (C_2H_5)_2S + C_2H_5Br$, but apparently decrease slightly with temperature for the reaction, $C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_3I$. $E_{\mathrm{obs.}}$ is abnormally high at 55° for the decomposition of triethylsulfine bromide in acetylene tetrachloride.

5. The results appear to indicate that (a) the energy of activation (critical increment) of isolated reactions in solution is independent of temperature, (b) deviations from constancy in $E_{\mathrm{obs.}}$ are due to abnormalities in the solvent.

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