pounds should not be over two degrees. Two angles of each of the new salts were measured and the results, together with those of Werther[3] on the double sulfates, and of Tutton on the thallous zinc selenate, follow:

Double Sulfates
$R''SO_4.TlSO_4.6H_2O$

R″	Angles	
	70° +	109° +
Fe	38′	24′
Zn	48′	12′
Ni	54′	6′
Mg	54′	6′

Double Selenates
$R''SeO_4.TlSeO_4.6H_2O$

R″	Angles	
	71° +	108° +
Zn	32′	28′
Mn	17′	48′
Cu	50′	54′
Mg	35′	25′
Co	28′	26′
Ni	34′	26′

The substitution of selenium for sulfur in these double salts causes an increase of about 40′ in the acute angles and a corresponding decrease in the obtuse angles.

Summary

New double selenates of thallous selenate and the selenates of copper, cobalt, nickel, magnesium and manganese are described, together with confirmatory analyses. Composition and crystal measurements show that the compounds are directly analogous to the corresponding double sulfates.

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THE KINETICS OF THE REACTION BETWEEN THE HALOGENS AND SATURATED ALIPHATIC KETONES IN DILUTE AQUEOUS SOLUTION[1]

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In order to test, effectively, current theories relating to reaction velocity and its variation with temperature, it is necessary to have available accurate measurements for a number of different reactions; for hydrolytic reactions such as sugar inversion or ester hydrolysis the results of hundreds of investigations are now available, but comparatively few complete investigations have been made of non-hydrolytic reactions, partly because these are often so complicated that the mechanism is uncertain or the presence of simultaneous reactions necessitates uncertain corrections.

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[3] Werther, *J. prakt. Chem.*, **92**, 128 (1864).

[1] The work included in this paper is from the thesis presented by Charles F. Fryling in fulfilment of part of the requirement for the degree of Doctor of Philosophy in New York University.

We selected the reaction between halogens and ketones for investigation because it is one of the few simple, non-hydrolytic reactions not complicated to any appreciable extent by simultaneous reactions.

Previous Work.[2]—The stoichiometric equation for the change may be written, $CH_3COCH_3 + I_2 = CH_3COCH_2I + HI$; other ketones may be substituted for acetone and the iodine may be replaced by chlorine or bromine without modifying the reaction. In neutral dilute aqueous solution the rate of change is exceedingly slow but since the reaction is catalyzed by hydrogen ions it gradually increases in speed owing to formation of halogen acid. The velocity is proportional to the concentration of ketone and to the concentration of the catalyzing acid but is quite independent of the concentration of the halogen; hence, Lapworth who first studied the reaction suggested that it was really an example of successive reactions and consisted of a slow primary change of the ketone (perhaps to the enolic form) under the influence of the hydrogen ions, followed by an almost instantaneous halogenation of the product. This may be written in the case of acetone and bromine as follows.

$$CH_3COCH_3 + H^+ = CH_3C(OH){:}CH_2 + H^+ \quad (1)$$
$$CH_3C(OH){:}CH_2 + Br_2 = CH_3C(OH)BrCH_2Br \quad (2)$$
$$CH_3C(OH)BrCH_2Br = CH_3COCH_2Br + HBr \quad (3)$$

Reaction 1 is slow and Reactions 2 and 3 are very fast. Dawson, who studied the reaction between ketones and iodine, endorsed the keto-enol transformation hypothesis. As ordinarily studied the concentrations of reactants are approximately 0.1 *M* ketone, 0.1 *N* acid and 0.01 *N* halogen; under these conditions the concentration of ketone and acid in any one experiment is practically constant and the halogen therefore disappears at a constant rate; also the reaction goes practically to completion except in the case of the higher ketones and iodine where the velocity of the back reaction, $RCH_2COCH_2I + I^- + H^+ = RCH_2COCH_3 + I_2 + H^+$, becomes appreciable when highly accurate measurements are being made. This is the only simultaneous reaction accompanying the main reaction which is, therefore, almost ideal in being free from secondary changes.

Acetone and the Halogens

Lapworth, who first studied the reaction between acetone and chlorine, found that the rate of disappearance of the chlorine was not independent of its concentration; during the early stages of the reaction the chlorine reacted at a distinctly greater rate than toward the end. Using ordinary reaction-velocity technique, we repeated and confirmed Lapworth's experiment; when however, we made the experiment using our improved technique, the chlorine behaved like the other two halogens and reacted at constant rate independent of its concentration. Evidently, the results obtained by the ordinary technique of pipetting and analyzing successive samples from a reaction vessel are vitiated by two errors due (1) to evaporation of the ketone and (2) to evaporation of the halogen. The second error would make the reaction appear faster, while the first would retard the reaction; in the case of bromine and iodine the two errors

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[2] (a) Lapworth, *J. Chem. Soc.*, **85**, 30 (1904). (b) Dawson and Leslie, *ibid.*, **95**, 1860 (1909). (c) Dawson and Wheatley, *ibid.*, **97**, 2048 (1910). (d) Dawson and Ark, *ibid.*, **99**, 1740 (1911).

approximately neutralize each other, but for the more volatile chlorine the second error is distinctly greater.

When we had completed the experiments for the three halogens we obtained the remarkable result that chlorine, bromine and iodine react with acetone with exactly the same velocity and the three reactions have exactly the same temperature coefficient (Table I).

TABLE I

REACTION BETWEEN ACETONE AND THE HALOGENS IN DILUTE AQUEOUS SOLUTION CATALYZED BY HYDROCHLORIC ACID[3]

	Chlorine	Bromine	Iodine
$k_{25} \times 10^4$ (±1.0%)	16.96	17.12	17.19
k_{25}/k_{20} (±0.2%)	1.819	1.818	1.818

Homologs of Acetone and Iodine[4]

In our preliminary experiments the values of k_{25}/k_{23} for a number of ketones were determined and the results are given in Table II. From this it will be seen that methylethyl ketone reacts about 25% faster than acetone, and methyl-*tert.*butyl ketone (pinacolin) reacts less than half as fast.

TABLE II

REACTION BETWEEN KETONES AND IODINE IN DILUTE AQUEOUS SOLUTION CATALYZED BY HYDROCHLORIC ACID

	k_{25} (±10%)	k_{25}/k_{23} (±0.2%)		k_{25} (±10%)	k_{25}/k_{23} (±0.2%)
Acetone	17	1.2668	Methyl-*iso*butyl	18	1.2612
Methylethyl	22	1.2667	Pinacolin	8	1.2631
Methylpropyl	..	1.2634	Ethylpropyl	18	1.2629
Methyl-*iso*propyl	..	1.2632	Mean	..	1.2633
Methylbutyl	..	1.2593			

$k_{25}/k_{23} = 1.2633$, gives $Q = 20{,}470$ and $k_{35}/k_{25} = 3.071$.

We purified both these ketones with great care by different methods so that we feel sure these differences are not due to impurities. The temperature coefficients of all the ketones are the same within experimental error. In order to test this last statement further we performed another series of experiments (Table III) using two temperatures 5° apart which enabled us to obtain more accurate values for the temperature coefficient; here again we found the temperature coefficients for all the ketones to be absolutely the same within the limits of experimental error, although the velocities varied appreciably.

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[3] The velocity constant given throughout this paper is the (calculated) rate of disappearance of halogen in moles per minute from a liter of solution containing 1 mole of ketone, 1 equivalent of hydrochloric acid, about 0.01 equivalent of halogen and 0.025 mole of potassium halide. The actual concentrations of reactions were approximately 0.1 *M* ketone, 0.1 *N* hydrochloric acid and 0.01 *N* halogen.

[4] The velocity constants obtained by Dawson and his co-workers are different from ours, the difference being probably due to impurities in their ketones. See Ref. 2 d.

TABLE III

REACTION BETWEEN KETONES AND IODINE IN DILUTE AQUEOUS SOLUTION CATALYZED BY HYDROCHLORIC ACID

	k_{30}/k_{25} (±0.2%)	k_{25}/k_{20} (±0.2%)	k_{25} (±2.0%)
Acetone	1.7750	1.8117	17.1
		1.8099	
Methylethyl	1.7750		20.9
Diethyl		1.7910	17.1
Methylpropyl		1.7955[a]	19.4
		1.7972[a]	
Methylbutyl	1.7752[a]		23.1
	1.7739[a]		
Pinacolin	1.7686[a]		7.7

[a] The back reaction necessitated the use of an approximation formula to find these values (see under Experimental Part). If $Q = 20,570$, then $k_{35}/k_{25} = 3.088$, $k_{30}/k_{25} = 1.774$ and $k_{25}/k_{20} = 1.809$.

Discussion

The fact that the rates of reaction of chlorine, bromine and iodine with acetone are exactly the same and completely independent of the concentration of halogen confirms Lapworth's view that the mechanism of the reaction consists of a slow initial reaction between acetone and hydrogen ion, followed by a very rapid reaction involving the halogen. It is doubtful, however, whether this slow initial reaction is really an enolization as represented by the equation, $CH_3COCH_3 + H^+ = CH_3C(OH):CH_2 + H^+$, for it is common experience in organic chemistry that the substitution of labile hydrogens by alkyl groups favors the keto form in keto-enol tautomers; such substitution therefore reduces the velocity of the change keto $\longrightarrow$ enol and consequently the homologs of acetone should react more slowly than acetone itself. With the exception of pinacolin, however, all the ketones react at the same rate as or faster than acetone. Furthermore, an experiment of Dawson and Powis,[5] in which they added iodine to a neutral solution of acetone and measured the change in conductivity, shows that there is no appreciable amount of the enolic isomer present in an aqueous solution of acetone. It seems desirable, however, to postpone further discussion of this point until some work now in hand is completed, on the mechanism of the back reaction, namely, the decomposition of iodo-acetone by hydrogen ion and the iodide ion.

This paper completes the study of the direct reaction, $CH_3COCH_3 + I_2 = CH_3COCH_2I + HI$. It has been shown that the temperature coefficient of the reaction is independent of the ketone, of the halogen and of the presence of neutral salts and non-electrolytes in the solution; the only way in which the temperature coefficient can be changed is by affecting the state of combination of the hydrogen protion (unhydrated hydrogen ion); by replacing a strong univalent acid by sulfuric acid in the presence

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[5] Dawson and Powis, *J. Chem. Soc.*, **101,** 1503 (1912).

of a sulfate[6] we can depress the temperature coefficient from its normal value, 3.08, to 2.55, the value obtained in ester hydrolysis.

Experimental Part

With a few modifications described later the apparatus and technique are similar to those described in a previous paper[7] so that the measurements of the temperature coefficient are correct to about ±0.2%. Reaction velocities may be obtained to the some high degree of precision but such a procedure necessitates careful determinations of acid and ketone concentration, and these refinements were not made; the reaction velocities are, however, accurate to ±2% unless otherwise noted. In the case of the materials used, except the ketones, the highest grade obtainable was purchased and used without further purification. It was found necessary in every case to purify the ketones carefully by 'chemical' methods, since distillation was found to be insufficient. A pure, saturated ketone will not perceptibly decolorize a dilute solution of permanganate in five minutes nor liberate iodine from a solution of hydriodic acid, and we considered a specimen of ketone sufficiently pure when it passed these two tests. It was necessary to submit all the ketones used to both of these tests because samples purchased and purified simply by distillation nearly always decompose permanganate and liberate iodine from hydriodic acid. All of the ketones used except pinacolin and ethylpropyl ketone were purified by converting them to the respective bisulfite compounds in the usual way. Pinacolin and ethylpropyl ketone do not form bisulfite compounds and we purified these through the semicarbazones, recovering the ketone by hydrolyzing with dil. sulfuric acid; we also purified a specimen of methylethyl ketone by this method.

In making our iodine titration we used as a source of light a 100-watt lamp bulb immersed in a blue starch-iodine solution; this was entirely satisfactory and made us independent of daylight. The buffer solutions used for stopping the reaction when ready for titration were mixed solutions of acetic acid and sodium acetate which had a Sörensen (P_H) value between 4 and 5.

It seems worth while to describe our method of measuring the temperature coefficients, since the method enables this important quantity to be measured with great ease and accuracy and renders unnecessary two separate experiments; the method is an improvement on that already described.[7] A solution of the ketone and halogen in convenient strengths is first prepared and analyzed accurately for the halogen; this gives the uncorrected initial titer. The mixture is then transferred by means of a dry siphon to two weighed, glass-stoppered cylinders of about 600cc.

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[6] Rice, Fryling and Wesolowski, This Journal, **46**, 2405 (1924).

[7] Rice and Kilpatrick, *ibid.*, **45**, 1401 (1923).

capacity and each cylinder with its contents is weighed. One cylinder is then transferred to a thermostat at 25° and the other to a thermostat at 30°; after the mixtures have reached the temperatures of the baths, the reactions are started by the addition of a known volume of acid which is at the same temperature as the reaction mixture; the time of addition of the acid is carefully noted. Before the final titrations, the reaction mixtures are transferred to small, glass-stoppered reaction flasks by means of fast running siphons, precautions being taken to avoid change in temperature during this operation; each of these flasks holds a sufficient amount of liquid for a titration. Previous experiments had shown that the reaction proceeds about 1.77 times as fast at 30° as at 25°; we find it best to make titrations of the two solutions at corresponding times; that is, if we titrate a sample from the 30° bath after t minutes we make a corresponding titration from the 25° bath after 1.77 t minutes; the reaction has progressed approximately to the same extent and the coefficients thus obtained are very constant. After obtaining the rate of disappearance of halogen per minute it is evident that the small corrections for the different densities of the solution can be readily applied, and the ratio of the two rates gives the temperature coefficient.[8]

Summary

1. In dilute aqueous solution chlorine, bromine and iodine react with acetone with the same velocity within ±1% and the three reactions have the same temperature coefficients within ±0.2%. This confirms the view that the mechanism consists of a slow reaction between acetone and hydrogen ion followed by a very rapid reaction involving the halogen.

2. Pinacolin and iodine react at less than half the rate of acetone and iodine; all the other ketones investigated react at the same rate as acetone, or at a higher rate. This does not support the hypothesis that the preliminary change is an enolization of the ketone.

3. The reactions between the different ketones and iodine all have the same temperature coefficient.

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[8] An additional correction is necessary for some of the higher ketones with which owing to the back reaction the rate of disappearance of iodine is not quite independent of its concentration; for these ketones the relation between time and iodine titer instead of being linear is slightly curved. In these cases we found empirical equations ($y = ax + bx^2 + cx^3$) for the curves and from these found the rate of disappearance of iodine during the early stages of the reaction when the back reaction was inappreciable.