The infrared spectra were obtained using solutions of the derivatives in chloroform for those compounds which were reasonably soluble in chloroform. For the other derivatives, the spectra were obtained using mulls in Nujol. All derivatives showed retention of the cyano group as demonstrated by characteristic absorption peaks in the 4.47-micron region. All derivatives showed at least some modification of the amino absorption bands in the 2.8 to 3.0-micron region in comparison with the spectra of the corresponding underivatized compounds. The acetyl, acid succinyl, succinyl, carbethoxy, and phenylcarbamyl derivatives showed characteristic carbonyl absorption bands in the 5.85 to 5.96-micron region. The Shiff base compounds showed no nitrogen to hydrogen absorption in the 2.8 to 3.0-micron region, but did show imino stretching absorption in the 6.1-micron region.

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Reaction of Hydrazine and Iodomethane

Removal of Iodomethane from a Gas Phase in Contact with Alkaline Hydrazine Solution

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The removal of iodomethane from the gas phase over alkaline solutions of hydrazine is a bimolecular interfacial reaction unretarded by the reaction products. The reaction was studied from 21° to 50.1° C. by a gas chromatographic technique from 0 to 0.77 mole fraction of hydrazine hydrate in the solution. The rate of disappearance of iodomethane from the gas phase is directly proportional to the concentration of iodomethane in the gas phase, the mole fraction of hydrazine hydrate in the solution, the interfacial area of the solution, and the reciprocal of the volume of the gas phase.

THE DIRECT reaction of macro amounts of alkyl iodides with hydrazine has been known for some time (*4*). Kinetic studies of the reaction of hydrazine and iodine have been reported (*8*) but not an investigation of the kinetics and mechanism of the iodomethane-hydrazine reaction.

This investigation is part of an effort (*6, 10*) now in progress to determine the mechanism and kinetics of the reaction between iodomethane and hydrazine. The application and verification of reaction models in predicting the behavior of iodomethane in the presence of reactive sprays in large columns and in defining reaction parameters is the primary goal of this project. These results cover the case where a gas phase, which contains a very low concentration of iodomethane, is in contact with an alkaline hydrazine solution.

EXPERIMENTAL

Iodomethane, iodoethane, and 95% hydrazine (Eastman Organic Chemicals) were used without further purification. The iodomethane and iodoethane were stored at 4° C. until needed. To obtain the desired initial concentration of iodomethane (ca. 20 mg. per cu. meter or ca. 4×10^{-3} torr) in the experiments, appropriate dilutions were made of the vapors saturated with iodomethane. The hydrazine stock solution was 93.4 ± 0.5 wt. % hydrazine. The direct iodate method (using solvent) described by Audrieth and Ogg (*1*) was used.

Alkaline hydrazine solutions were prepared by dilution of the hydrazine stock solution and standardized sodium hydroxide solution. There was no indication of deterioration of the alkaline hydrazine solution stored at ambient conditions during the course of the experiments.

A Research Specialties gas chromatograph equipped with a Warner Chilcot electron-capture detector was used. The column was either a 6- or 12-foot length of 0.25-inch I.D. column packed with 20% SE 30 on Chromosorb-P (60- to 80-mesh) and was operated under isothermal conditions (ca. 60° C.). Nitrogen was the carrier gas at flow rates of ca. 100 ml. per minute.

The electron-capture detector used a Sr^{90} source and was compatible with water vapor, which was present in the aliquots of the gaseous reaction mixtures.

The reaction cells consisted of two types. Both types of cells were jacketed borosilicate glass vessels. The first type of vessel was cylindrical with an I.D. of 2.7 cm. and a volume of 55.3 ± 0.1 ml. Access to the interior of the reaction vessel was through a 6-mm. I.D. tube located at the top of the vessel. The system was sealed with a rubber serum bottle stopper. Iodomethane was absorbed by the rubber stopper, but both the rate and extent of absorption were negligible during the time of observation of a reaction. In smaller reaction vessels where the ratio of surface area of rubber to glass is larger by a factor of 10 than in the vessel used in these studies, the extent of iodomethane absorption was appreciable.

The second type of reaction cell differed from the first in that the top of the cell consisted of a 24/40 standard taper joint. This joint provided an entrance to the interior of the reaction vessel so that tubes of varying cross sectional areas could be placed in the reaction vessel.

The reactions were started by the addition of a volume of gas containing iodomethane through a rubber stopper with a microsyringe. Aliquots for the determination of iodomethane were withdrawn through this stopper. Normally 10 to 15 10-μl. aliquots of gas were withdrawn when the reaction was followed to 90 to 99% of completion. Sometimes additional 500-μl. aliquots were taken to better define the gas phase concentration of iodomethane when less than 10% of the iodomethane remained. The 10-μl. aliquots removed only a negligible amount of iodomethane from the reaction vessel. The 500-μl. aliquots removed approximately 1% of the iodomethane which remained in the gas phase at the time the aliquot was taken.

The reaction vessels were maintained at a specified temperature by circulation of ethylene glycol-water mixture from a thermostated temperature bath through the jacket of the reaction vessel. The temperature in the reaction vessel was constant within ±0.05° C.

Calibration of the detector showed that detector response was linear for aliquots which contained up to 6×10^{-4} μg. of iodomethane. Both the peak area and the peak height were directly proportional to the amount of iodomethane for aliquots which contained less than this amount of iodomethane. Proper choice of aliquot size permitted the concentration of iodomethane to be determined from 4×10^{-3} to 56 mg. per cu. meter. The detector was less sensitive to iodomethane than to iodomethane. The minimum detectable amount of iodoethane was 3×10^{-4} μg. compared with 2×10^{-6} μg. for iodomethane. The detector response was linear in the case of iodoethane up to 8×10^{-3} μg. The accuracy of the determination of iodomethane was estimated to ca. 7%. The precision of the determination of iodomethane was 3.6%.

RESULTS

The gas phase reaction of iodomethane with hydrazine at 50° C. was slow compared with the reaction at the interface of the gas phase and the solution. This was determined by placing an amount of hydrazine equivalent to a pressure of 12 torr in the reaction vessel. The iodomethane was added to obtain a pressure of ca. 4×10^{-3} torr and only ca. 10% of the iodomethane disappeared over a 1.2-hour time interval.

The heterogeneous reaction was first order with respect to the concentration of iodomethane. A plot of the logarithm of the peak height due to iodomethane *vs.* the reaction time is shown in Figure 1. The linearity of these data over a 100-fold change in concentration shows that the reaction is first order with respect to the iodomethane concentration. The rate of the reaction is described by the pseudo first order rate constant, k_{obsd}

$$-\frac{d \ln n}{dt} = k_{\text{obsd}} \qquad (1)$$

where n is the concentration of iodomethane and t is the time.

The peak height for the first two aliquots in Figure 1 fall below the extrapolated linear relationship. This is explained by the incomplete mixing of the iodomethane for the first few minutes after its addition. The extrapolated value of peak height at a reaction time of zero was within 2 to 3% of this extrapolated value for similar dilutions in other experiments. The agreement of extrapolated peak heights was also valid for similar dilution when the hydrazine composition of the solution was changed and a different rate of reaction was found.

The effect of changing the volume of the gas phase was determined in a series of experiments where all other parameters except the volumes of the gas phase and of the solution were kept constant. The results of this series of experiments are given in Table I.

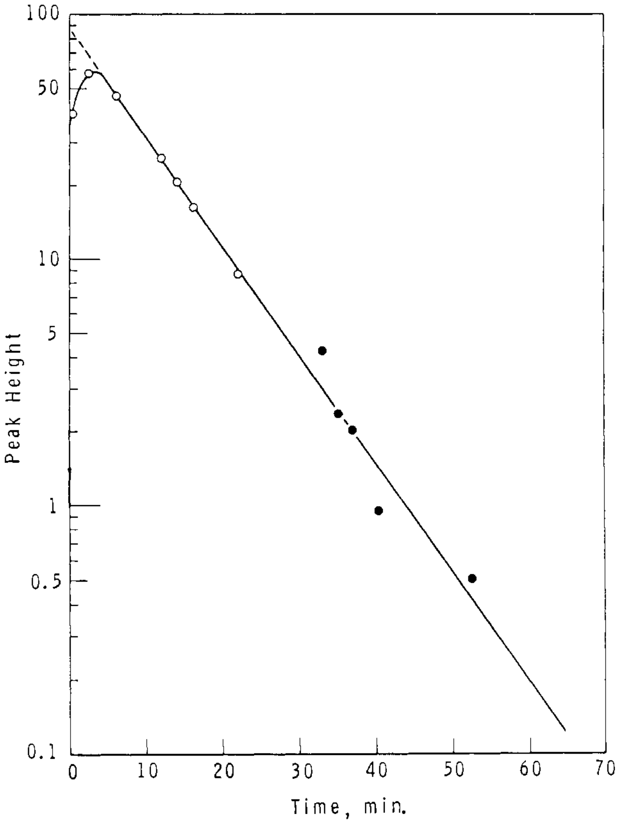

Figure 1. Peak height (relative concentration) of iodomethane vs. reaction time

Attenuation factor, 100X; initial iodomethane concentration, 19 mg./cu. meter; temperature, 50.1° C.; 46.8 wt. % N_2H_4 (0.50 mole fraction N_2H_5OH); 0.050*M* NaOH; $\tau_{1/2}$, 6.7 minutes; k_{obsd}, 0.104 minute^{-1}

○ 10-μl. aliquots

● 100-μl. aliquots

Variation of the surface area of the solution was accomplished by the use of the second type of reaction vessel. This reaction vessel permitted 3- and 8-mm. I.D. tubes, which contained alkaline hydrazine solution, to be placed in the vessel. The miniscus of the solution in tubes of this small diameter give rise to an uncertainty in the determination of the surface area of the solution in the tubes. The value of k_{obsd} was doubled when two of the tubes were present both in the case of the 3- and 8-mm. I.D. tubes. A summary of the effect of the gas phase volume, sodium hydroxide concentration, mole fraction of hydrazine hydrate, and interfacial area is presented in Table II. The

Table I. Effect of Volume of the Gas Phase on the Observed Rate of Reaction[a]

Gas Phase Volume, Ml.	k_{obsd}, Observed Rate Constant Min.$^{-1}$	k_{obsd} V, Min.$^{-1}$ Ml.
45.4	0.079	3.58
32.9	0.112 ± 0.007	3.59
27.9	0.134 ± 0.003	3.74
22.9	0.161	3.59
12.9	0.277	3.57

[a] Mole fraction hydrazine hydrate in the solution, 0.212, initial iodomethane concentration in the gas phase, ca. 30 mg. per cu. meter, temperature 50.1° C., calculated interfacial area 5.8 sq. cm.

Table II. Effect of Hydrazine and Hydroxide Concentration on the Observed Rate of Reaction[a]

Mole Fraction Hydrazine Hydrate	Molarity NaOH, *M*	Calculated Cross Sectional Area at Interface, Sq. Cm.	Volume Gas Phase, Ml.	k_{obsd}, Observed Rate Constant Min.$^{-1}$	($k_{obsd}V/A$), Min.$^{-1}$ Cm.
0	0.0504	5.65	51.3	5.4×10^{-4}	4.9×10^{-3}
0.11	0.0504	5.65	51.3	3.0×10^{-2}	0.273
0.11	0.2015	5.65	51.3	2.8×10^{-2}	0.254
0.14	0.0504	3.6	54.3	$(2.9 \pm 0.6) \times 10^{-2}$	0.44
0.27	0.0504	4.72	53.3	$(6.0 \pm 0.2) \times 10^{-2}$	0.68
0.27	0.2015	4.72	53.3	$(5.8 \pm 0.2) \times 10^{-2}$	0.65
0.50	0.0504	5.65	51.3	1.04×10^{-1}	0.95
0.50	0.0504	3.6	54.3	$(1.1 \pm 0.1) \times 10^{-1}$	1.70
0.50	0.0504	0.5[b]	74	$(7.8 \pm 0.5) \times 10^{-3}$	1.08
0.77	0.0504	5.65	51.3	$(1.7 \pm 0.2) \times 10^{-1}$	1.6

[a] Temperature 50.1° C., initial iodomethane concentration in the gas phase (air) of ca. 30 mg./cu. meter. [b] The Type II reaction vessel was used with the solution in 8-mm. I.D. tubes. Wetting of the walls caused the interfacial area to be approximately twice that of the cross sectional area of the tube.

product, ($k_{obsd}V/A$), where V is the gas phase volume and A is the interfacial area is shown as a function of mole fraction hydrazine hydrate in Figure 2. The comparison of data with an interfacial area of 5.65 sq. cm. is excellent. The slope of this line is 2.0 minute^{-1} cm. (mole fraction hydrazine hydrate)$^{-1}$. With the exception of the 3.6 sq. cm. interfacial area values, the data is in good agreement with a value for the slope of 2.3 ± 0.3 minute^{-1} cm.$^{-1}$ (mole fraction hydrazine hydrate)$^{-1}$.

The products of the reaction represented by Equation 2 are assumed to be monomethylhydrazine hydrate and iodide ion for the alkaline environment. The competitive reaction of the

$$N_2H_5OH + CH_3I + OH^- \rightarrow (CH_3)NHNH_3OH + H_2O + I^- \quad (2)$$

monomethylhydrazine hydrate with iodomethane represented by Equation 3 was assumed to be small because of the extremely low concentration of monomethylhydrazine hydrate which is produced by the first step of the reaction.

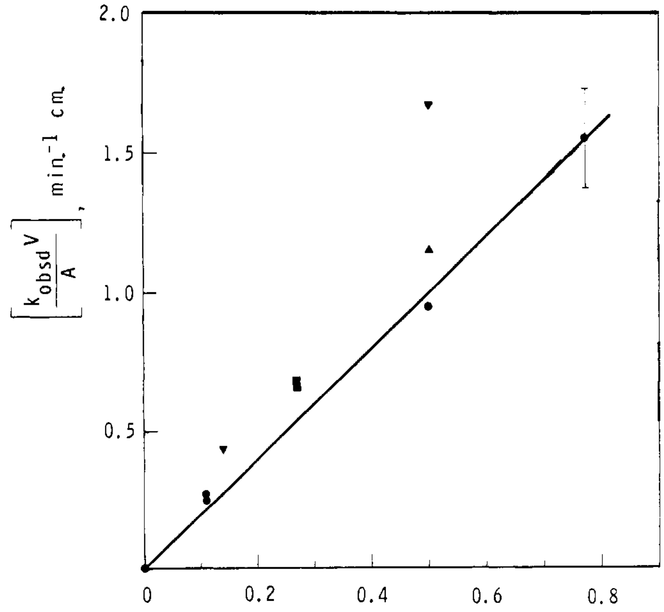

Figure 2. Rate constant, $[k_{obsd}V/A]$ as a function of mole fraction hydrazine hydrate

Temperature 50.1° C.

● 5.65 sq. cm. interfacial area

■ 4.7 sq. cm. interfacial area ▼ 3.6 sq. cm. interfacial area

$$(CH_3)NHNH_3OH + CH_3I + OH^- \rightarrow (CH_3)_2NNH_3OH + H_2O + I^- \quad (3)$$

This is in contrast to the relative importance of this reaction when higher concentrations of iodomethane are initially reacted with hydrazine (*1*). The products of the reaction had no effect on the rate of disappearance of iodomethane in the concentration range of this study. This was shown by experiments where a hydrazine solution, which had been used previously, was used in a second experiment. Also, the use of nitrogen instead of air in the gas phase had no effect on the rate of disappearance of iodomethane over the solutions of hydrazine.

Iodoethane instead of iodomethane was used in one experiment where the hydrazine hydrate mole fraction in the solution was 0.77 and the molarity of NaOH was 0.050*M*. At 50.1° C. and a gas phase volume of 51.3 ml., the observed pseudo first order rate constant was 0.0925 minute^{-1}. The initial concentration of iodoethane in this experiment was 800 mg. per cu. meter.

Table III presents the values of k_{obsd} for the heterogeneous reaction of methyl iodide and a 0.50 mole fraction hydrazine hydrate solution at several temperatures where the other parameters were kept constant.

DISCUSSION

These studies were originally designed on the premise that the reaction was primarily a gas phase reaction of iodomethane with hydrazine. The liquid phase was necessary to obtain a rapid decrease in the gas phase concentration of iodomethane. The rate of reaction of iodomethane and hydrazine in the gas phase was slow when compared with the rate of the heterogeneous reaction. The possibility of a gas phase diffusion-controlled reaction was considered but was discarded when sampling of the gas phase at different heights above the solution gave the same rate of disappearance of iodomethane.

Table III. Effect of Temperature on the Observed Rate of Reaction[a]

Temp., ° C.	k_{obsd}, Min.$^{-1}$
50.1	0.112 ± 0.009
40.0	0.082 ± 0.005
35.0	0.077
32.4	0.066
21.2	0.059

[a] Mole fraction hydrazine hydrate, 0.50, NaOH concentration, 0.0504*M*, calculated cross sectional area at interface, 3.6 sq. cm., volume gas phase, 54.3 ml.

The rate of disappearance of iodomethane is proportional to the concentration of iodomethane, the reciprocal of the volume of the gas phase, and the interfacial area of the hydrazine solution and the gas phase.

The most difficult to determine or to control of these parameters in the experiments performed was the interfacial area. This was due to the wetting of the glass walls. The author assumed that the interfacial area was constant when the volumes of liquid were equal. Attempts to calculate the cross sectional area of the reaction vessel from the geometry and dimensions of the vessel yielded only approximations to the interfacial area of the solution. The interfacial area was somewhere between the calculated cross sectional area for small volumes of liquid in the reaction vessel and the cross sectional area for larger volumes of liquids in the vessel. Table II presents the results of several experiments, which were designed to give the effect on k_{obsd} of the variation of either hydrazine or hydroxide concentration. By consideration of the experiments where the calculated cross sectional area was constant, the effect of variation of either the hydrazine or hydroxide concentration can be determined. The two sets of data where the hydroxide concentration was either 0.0504 or 0.2015*M* showed a slight decrease of 4 and 7% in the k_{obsd} for the 0.27 and 0.11 mole fraction hydrazine hydrate solutions, respectively.

The rate of disappearance of iodomethane was proportional to the mole fraction of hydrazine hydrate in the solution. Attempts to correlate k_{obsd} with the molarity or the activity of hydrazine produced only nonlinear relationships. The activity of hydrazine was calculated from the vapor-liquid composition data of Burtle (*3*). These data were for the system hydrazine-water and were used to obtain the activity of hydrazine in the solution. The gas phase hydrazine was assumed to be completely dissociated, so that the ratio of partial pressure of hydrazine, as determined by Burtle, to the vapor pressure of pure hydrazine at that temperature is the activity of hydrazine in the solution. The activity of hydrazine can be determined by graphical interpolation. The effect of hydroxide concentration, 0.05 to 0.20*M* in this study, on the hydrazine activity was ignored in the correlation of k_{obsd} and hydrazine activity. The effect of hydroxide on the ionization of hydrazine hydrate would be small although there would be a somewhat more appreciable effect on the activity of water, which would cause a greater relative concentration of hydrazine compared with hydrazine hydrate than if hydroxide ion were not added. When the correlation was made of k_{obsd} with the mole fraction of hydrazine hydrate, a direct proportionality was found when both the interfacial area and gas phase volume were kept constant. In an aqueous solution, hydrazine would be present as the hydrate—i.e., N_2H_5OH. Since the pK for hydrazine hydrate is ca. 5.8 (*9*), the hydrazine hydrate would be present primarily in the associated form in an alkaline solution.

These results are explained in the following reaction scheme. The number of molecules of iodomethane reacting in unit time, dN/dt, is

$$-\frac{dN}{dt} = k_fAf(n) \tag{4}$$

where A is the area of the interface between the gas phase and solution, $f(n)$ is the number of molecules of iodomethane which strike the interface in unit time, and k_f is the fraction of molecules which strike the interface and react. The term (*7*), $f(n)$, is given by

$$f(n) = nN_0\left[\frac{kT}{2\pi m}\right]^{1/2} \tag{5}$$

where n and m are the concentration and mass of iodomethane, T is the absolute temperature, k is the Boltzmann constant. Substitution into Equation 3 of

$$n = nVN_0 \tag{6}$$

where V is the volume of the gas phase and N_0 is Avogadro number, obtains by rearrangement

$$-\frac{dn}{dt} = \frac{k_fA}{VN_0} \cdot f(n) \tag{7}$$

Combination of Equations 4 and 6 gives

$$-\frac{1}{n}\frac{dn}{dt} = -\frac{d\ln n}{dt} = \frac{k_fA}{V}\left[\frac{kT}{2\pi m}\right]^{1/2} \tag{8}$$

When Equation 7 is compared with the form of the equation which was obtained experimentally

$$-\frac{d\ln n}{dt} = k_{\text{obsd}} \tag{1}$$

an expression for k_{obsd} is obtained.

$$k_{\text{obsd}} = \frac{Ak_f}{V}\left[\frac{kT}{2\pi m}\right]^{1/2} \tag{9}$$

The effect of volume on the rate of disappearance of iodomethane at constant interfacial area is shown in Table II. The constancy of the term, $k_{\text{obsd}}\ V$, is in good agreement with Equation 9. Rearrangement of Equation 9 into the form which the data in Table II and Figure 2 are presented gives

$$k_f\left[\frac{kT}{2\pi m}\right]^{1/2} = k_{\text{obsd}}\frac{V}{A} \tag{10}$$

k_f is $(7 \pm 1) \times 10^{-6}$ when experimentally determined values are substituted into Equation 10. A value of 5.5×10^3 cm. per second was used for $(kT/2\pi m)^{1/2}$ of iodomethane at 50.1° C.

The model which has been presented is a simple picture considering only the iodomethane striking the surface and either being retained by interface (reaction) or returning to be bulk of the gas phase (no reaction). The actual mechanism of reaction at the interface or the subsequent fate of iodomethane in solution was not needed in the treatment of the removal rates of iodomethane by this simple picture.

A somewhat more sophisticated model is obtained by consideration of the iodomethane diffusing into and reacting with the solvent. When the assumption that the gas phase is well mixed and is in equilibrium with the interface is made, the following relationship between a pseudo first order liquid reaction rate constant, k_1, and the observed rate of removal of iodomethane from the gas phase is obtained. (The amount absorbed per unit area up to time t, Q is given by

$$Q = C^*\left[\frac{D}{k_1}\right]^{1/2}\left[(k_1t + 1/2)\ \text{erf}\ [k_1T]^{1/2} + \left[\frac{k_1T}{\pi}\right]^{1/2} e^{k_1t}\right]$$

which for $t >>$ seconds reduces to

$$Q = C^*\ [Dk_1]^{1/2}t$$

where C^* is the average liquid concentration at the interface. The quantity absorbed per unit area is

$$Q = (C_g^0 - C_g)\frac{V}{A}$$

where C_g^0 and C_g are the gas phase concentrations at time zero and t. The partition coefficient is

$$\beta = \frac{C}{C_g}$$

When 50% of iodomethane has been absorbed, the time is the half time for removal, $\tau_{1/2}$, and

$$\tau_{1/2} = \frac{0.693}{k_{\text{obsd}}}$$

Substitution yields

$$(C_g^0 - \tfrac{1}{2} C_g)\frac{V}{A} = 0.75\, \beta\, C_g [D k_1]^{1/2} \left(\frac{0.693}{k_{\text{obsd}}}\right)$$

which by rearranging and squaring results in Equation 11.)

$$k_1 = \frac{2.57 \times 10^{-4}}{\beta^2 D} \left[\frac{k_{\text{obsd}} V}{A}\right] \tag{11}$$

where β is the partition coefficient (concentration of iodomethane in liquid per concentration of iodomethane in gas phase), D is the diffusivity of iodomethane in the liquid (square centimeters per second), and the other quantities have already been defined. The partition coefficient of iodomethane between water and air has been determined in this laboratory to be 1.5 at 50° C. for very dilute solutions of iodomethane. The diffusivity of iodomethane was assumed to be 2.5×10^{-5} sq. cm. per second, which is of a correct order-of-magnitude value when compared with the diffusivity of various haloalkanes (*5*).

The liquid reaction rate constant which is calculated from the data in Table II is proportional to the square of the mole fraction of hydrazine hydrate in the solution (Equation 11 and Figure 2) for the concentration range which was studied. The calculated liquid reaction rate for a 5.1-mole per liter solution—i.e., 0.11 mole fraction—is 0.34 second^{-1} which corresponds to a second order rate constant of 0.07 liter mole^{-1} second^{-1}.

The liquid reaction rate constant is estimated to be ca. 0.3 liter mole^{-1} second^{-1} which is a factor of four faster than that calculated by use of Equation 11. (The liquid reaction rate constant has been determined directly in this laboratory to be 0.02 liter mole^{-1} second^{-1} at 21° C. for 0.03 to 0.1*M* hydrazine solutions which are 0.05*M* in sodium hydroxide. With the assumption of an activation energy of 18 kcal. per mole, the reaction rate constant at 50° C. is calculated to be 0.3 liter mole^{-1} second^{-1}.) The experimental dependence of k_1 calculated by Equation 11 on the square of the mole fraction of hydrazine hydrate is quite unexpected and is difficult to rationalize with respect to the second order kinetics which were found for dilute (ca. 0.1*M*) hydrazine solutions. The application of Equation 10 to prediction of rates of iodomethane removal appears to be more reliable than the predicted rate from the diffusion-reaction model.

Treatment of the data in Table III according to the Arrhenius relationship yields an energy of activation of between 5 and 6 kcal. per mole. The energy of activation appears to increase as the temperature is increased. Winning (*11*), in studying the heterogeneous reaction of hydrazine and oxygen, found an energy of activation of 6.4 kcal. per mole which increased as the temperature was increased. Winning suggested that this effect, the increase in energy of activation, was due to the increasing importance of the gas phase reaction. Bowen has reported the energy of activation of the gas phase reaction of hydrazine and oxygen to be 38 kcal. per mole (*2*). This reasoning could be applied to the reaction between hydrazine and iodomethane, and the rate of the gas phase reaction would be predicted to become an increasingly important term as the temperature is increased. (If 5 and 38 kcal. per mole are assumed to be the energy of activation of the first and second terms, and if at 50° C., the contribution of the second term to the over-all rate is 1%, then at 60° and 70° C., the contribution of the second term would be 5 and 24%, respectively.)

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Half Amides and Imides of *cis*-Cyclohexane-1,2-dicarboxylic Acid and *cis*-4-Cyclohexene-1,2-dicarboxylic Acid

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THE *cis*-cyclohexane-1,2-dicarboxylic anhydride [m. p. 31° C.; b.p. 161.7–1.9° C. (25 mm.)] and *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (m.p. 103–4° C.) are readily available commercial materials finding use as alkyd, polyester, and epoxy resin intermediates (*2, 3, 16*). The former is prepared by hydrogenating the latter (*13*), which is made by adding maleic anhydride to butadiene (*4, 6*).

Although many miscellaneous half amides and imides have been prepared from these anhydrides, only the *N*-alkyl imide derivatives have been given extensive study (*17, 19,*