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Chemistry of the KALC Process The $\text{CO}_2\text{-I}_2\text{-CH}_3\text{I-H}_2\text{O}$ System

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ABSTRACT

The chemistry of the CO₂-I₂-CH₃I-H₂O system in stainless steel has been investigated with respect to the probable reactions of these components in the KALC process. Iodine is stable in dry CO₂ contained in stainless steel; but in the presence of organic impurities or water, it is lost from solution via reactions which produce solid phases. Methyl iodide, however, is stable in either wet or dry CO₂ solutions. Distribution coefficients for I₂ and CH₃I between gas and liquid CO₂ have been measured from -26 to +30°C; they show that the solutes favor the liquid phase as the temperature is lowered. The corrosion loss of I₂ in the presence of 10 to 200 ppm H₂O has been followed as a function of time at 0 and +21°C. Weak associations between CO₂ and I₂, CO₂ and H₂O, and I₂ and I₂ can account for shifts in their respective distribution coefficients, but these associations are not strong enough to produce isolable phases. The occurrence of a weak CO₂·H₂O molecular species in the vapor is demonstrated by the near-infrared vibrations of the water group in the species.

INTRODUCTION

The primary chemistry of the KALC¹ process is the krypton distribution in liquid-vapor CO₂. Secondary chemistry involves the interaction of impurities, CO₂, and the containment system. Impurities will likely include fission product iodine and tritiated water, and the chemistry of these materials in CO₂ solutions has heretofore been virtually unexplored. The work reported here was concerned with chemical reactions in CO₂-I₂-CH₃I-H₂O systems in stainless steel containment which might alter the performance of the KALC process. Specific questions about the chemistry of these systems were: (1) How stable are molecular I₂ and CH₃I in a CO₂ solution contained in stainless steel? (2) How do molecular I₂ and CH₃I distribute between the gas and liquid phases of CO₂? (3) What are the effects of H₂O on the stability of I₂ and CH₃I in CO₂? (4) Will combinations of these materials cause corrosion of

stainless steel? (5) Will reaction or corrosion products possibly interfere with the KALC process? These questions are answered in this report, but we emphasize that the limited support and time available for this work could not result in a complete analysis of the secondary chemistry in the KALC process.

Physical properties of the $\text{CO}_2\text{-I}_2\text{-CH}_3\text{I-H}_2\text{O}$ systems (solubility limits, distribution coefficients, mass transfer phenomena, etc.) frequently limited the temperature range in our studies, and we could only cover the range of -26 to $+30^\circ\text{C}$. Furthermore, it was necessary to study some concentrations of I_2 , CH_3I , and H_2O greater than those anticipated in the KALC process in order to maintain good analytical sensitivities. However, we have sought to provide enough data in both of these circumstances so that a valid extrapolation to KALC conditions can be made.

EXPERIMENTAL

Most of the experimental work was performed in a high-pressure spectrophotometer cell fabricated from type 304 stainless steel. A simplified sketch of the cell is shown in Fig. 1. The cell was essen-

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Fig. 1. High-pressure spectrophotometric cell for liquid CO_2 experiments.

tially a jacketed cylinder capped on both ends with removable flanges. All seals, including those at the windows, were eventually made with Teflon O-rings to prevent reaction between the reagents and the rubber elastomer seals (see the Initial Experiments section of Results and Discussion below). Two silica windows were located on each flange assembly so that absorption spectra of both the liquid and the vapor regions could be measured when the cell was half-filled with liquid CO_2 . Because the distribution of I_2 favored the CO_2 liquid phase, the optical pathlength in the liquid was shortened by using tube extensions which protruded into the cell space. These additions to the flanges reduced the liquid pathlength from 34.42 cm to 1.81 cm, while the vapor pathlength remained at 34.42 cm. The resulting balance of liquid and vapor absorbance² values contributed substantially to the accuracy of the distribution coefficient measurements. Operating pressures comparable to the CO_2 vapor pressure at 30°C (approximately 1000 psia) were safely maintained in this cell.

The cell temperature was monitored continuously with an iron-constantan thermocouple embedded in the cell wall. A temperature profile of the cell interior was determined by calibration with thermocouples inserted through metal plugs in the window ports, with the cell half-filled with liquid CO_2 . It was found that the flanges usually ran at least 0.2°C warmer than the other parts of the cell at 0 to -20°C, which accounted for some transport of I_2 (see footnote 13) to the flanges.

The cell was refrigerated by circulating cold methyl cyclohexane through the cooling jacket from a reservoir within a Lauda Ultra Kryomat K 120 refrigerator. It was possible to reach temperatures of -50°C with this system, but frequently the concentration of solute in the liquid and/or gas phase at subzero temperatures was less than the sensitivity limit of the spectrophotometer. Consequently, much of the work was performed at 0°C and extrapolated to lower temperatures and concentrations.

The high-pressure cell fit in a Cary 14 recording spectrophotometer specially equipped with a vacuum-enclosed sample compartment that provided an insulated, moisture-free environment for the refrigerated cell. Absorption spectra of the liquid and vapor phases could be measured

separately by manually shifting the cell to position either phase in the sample light beam.

Reagents

Mallinckrodt AR grade I_2 and Eastman reagent chemical CH_3I (bp 41 to 43°C) were used directly from their respective containers. Matheson (Coleman instrument grade) 99.99 mole % pure CO_2 with a dew point better than -75°F was customarily dried in 1- to 2-liter batches over P_2O_5 in a stainless steel storage cell. Some later experiments were performed with undried CO_2 to determine any positive effects from the drying operation. These results are discussed in the Corrosion Study section below.

Procedure

The experimental procedure involved the assembly of the cleaned cell in an N_2 -purged glove bag, after the components had dried for at least 20 hr at 150°C. A charge of approximately 0.1 g of I_2 was then added to the cell, and the cell was sealed and half-filled with CO_2 liquid (approximately 0.3 liter) by condensing vapor from a supply bottle. Often, however, I_2 was introduced by condensing an I_2 -saturated CO_2 distillate in the spectrophotometer cell and diluting with pure CO_2 as necessary. For the corrosion studies, 1 to 100 μl of water was introduced directly into the bottom of the cell from a micropipette during cell assembly. This procedure was later modified by encapsulating the water in a glass ampule which subsequently was broken after the cell had been thoroughly equilibrated at a given temperature.

Method of Analysis — Spectral Measurements

Absorption spectra were measured from 200 to 2500 nm (the near-ultraviolet, visible, and near-infrared regions) on a Cary 14 recording spectrophotometer. All of the solution components, namely, I_2 , CH_3I , H_2O , and CO_2 , had thoroughly documented absorption bands in these regions. Table 1 shows the position and molar extinction coefficients

Table 1. Absorption bands used in the determination of component concentrations

	Band position ^a (nm)		ϵ^b (liters mole ⁻¹ cm ⁻¹)	Nature of transition
	Liquid	Vapor		
I ₂	510	520	778	Electronic
CH ₃ I	251	257	384 ^c	Electronic
H ₂ O	1880	1880	4 ^d	Vibration (overtone or combination)
	1380	1380		Vibration (overtone or combination)
CO ₂		1882	0.35×10^{-3}	Vibration (overtone or combination)
		1605	4.56×10^{-3}	Vibration (overtone or combination)
		1575	5.47×10^{-3}	Vibration (overtone or combination)
		1440	1.05×10^{-2}	Vibration (overtone or combination)

^aFor the CO₂ liquid or vapor medium.

^b ϵ = molar extinction coefficient. See footnote 2.

^cValue measured over pure CH₃I with no CO₂ present.

^dValue determined for liquid but applies as well to the vapor. See discussion in text on Novel Species.

of the bands that were monitored and the nature of the transition involved.

Iodine has several electronic transitions which give rise to absorption bands in the visible region,³ the principal one occurring at 520 nm. Large shifts in the position of this band are caused by solvation of the I₂ species, which have been used⁴ as a means of studying solute-solvent interactions. (Note the shift in the positions for I₂ liquid and vapor absorption bands.) The occurrence of I₄ molecules has been reported⁵ and is expected to give rise to a band in the near-uv at 290 nm (but this wavelength would also be subject to solvation shifts).

Methyl iodide has a molar extinction coefficient, ϵ , of 384 liters mole⁻¹ cm⁻¹ at 258 nm in the pure vapor. A corresponding value for CH₃I in CO₂ liquid and vapor was not measured because the distribution coefficient expression canceled this term (provided the values of ϵ were equivalent for both phases). A typical spectrum of CH₃I in the vapor over a CO₂ solution is illustrated in Fig. 2. Carbon dioxide has a series of vibrational overtone and combination bands which extend throughout the near-infrared region (700 to 2500 nm), the strongest of which occur between 1900 and 2100 nm. A very weak CO₂ band occurs at 1882 nm (assigned to $\nu_1\nu_2\nu_3 = 0,1,2$)⁶ and heretofore has received scant mention.⁷ Water likewise has vibrational combination and overtone bands in the near-infrared region. The principal ones used in this work were at 1380 and 1880 nm.

Fig. 2. Methyl iodide vapor over liquid CO₂ solution at 0°C.

RESULTS AND DISCUSSION

The experimental work was divided into three phases, or tasks, which involved the measurement of: (1) I_2 and CH_3I distribution coefficients between gas and liquid CO_2 , (2) corrosion reaction of CO_2 - I_2 - H_2O and CO_2 · CH_3I · H_2O with stainless steel, and (3) novel reaction products from CO_2 , H_2O , CH_3I , or I_2 . Prerequisites to these tasks were, however, the attainment of stable I_2 - CO_2 solutions and the control of the water content of CO_2 . These prerequisites were considered in the initial experiments.

Initial Experiments

The stability of I_2 in liquid CO_2 remained in doubt up until this work, and it was imperative to resolve this uncertainty before meaningful experiments on I_2 corrosion loss, compound formation, etc., could be performed. In some earlier studies, liquid CO_2 was found to swell the Buna N O-ring seals used in the cell and to leach a light oil from the rubber. With I_2 added to the CO_2 , a reaction between the I_2 and oil occurred causing I_2 loss from solution and the formation of an oily product which contained iodine. Replacement of the rubber seals with Teflon effectively eliminated any evidence of I_2 loss. When the clean systems were ultimately opened and the residue left in the cell after the venting of the CO_2 was examined by x-ray analysis, only crystalline I_2 was identified. These experiments demonstrated that I_2 and CO_2 form no unusual reaction products (either via reaction with themselves or with stainless steel), as was previously suggested,⁸ and that residues obtained by earlier workers were probably due to reaction products involving the sealants employed.

Water concentrations in liquid and gaseous CO_2 were previously determined⁸ by monitoring the 1880-nm combination band of H_2O ($\nu_2 + \nu_3$).⁹ With Matheson "bone dry" or "Coleman instrument" grade CO_2 , it was always observed that the band at 1880 nm reached a minimum intensity which could not be further reduced even by prolonged contact with desiccants such as P_2O_5 . From previously measured ϵ values¹ for H_2O , it was concluded⁸ by the authors that the minimum was equivalent to 6 to 8 ppm

H₂O. However, this water content is unusually high in view of the efficiency of P₂O₅ as a desiccant and leads one to consider additional contributions to the 1880-nm band.

The host of overtone and combination bands of CO₂ in the near ir suggest the possibility that a very weak CO₂ band might be overlapping the water band, and that after the CO₂ is dried, there remains some absorption due to the CO₂ itself. A calculation to estimate the energy of various arbitrarily chosen combination and overtone bands of CO₂^{9,10} verified the (0,1,2)⁶ band near 1880 nm. Taking anharmonicity effects into account, the (0,1,2) combination band gave a calculated energy of 5350 cm⁻¹ (1864 nm), which corresponded very closely to that of the measured transition at 5314 cm⁻¹ (1882 nm). Most references on CO₂ spectra, however, fail to mention the occurrence of a (0,1,2) combination band, probably because it is approximately 100 times weaker ($\epsilon = 3.47 \times 10^{-4}$ liter mole⁻¹ cm⁻¹) than its neighboring bands [e.g., (0,4,1)] and therefore appears only at high CO₂ densities, such as in the liquid, or at very long pathlengths. The work of Herzberg et al.⁷ substantiates the existence of the (0,1,2) band but does not pinpoint its position. Therefore the above calculation best locates the band. Additional evidence for the overlapping CO₂ band was found when the liquid pathlength was increased to the point where the band profile could be examined. It was found to be quite symmetrical, with a half-width of 14 cm⁻¹, and was clearly in contrast to that of the water band.

We conclude that the (0,1,1) band of H₂O and the (0,1,2) band of CO₂ overlap to the extent that trace H₂O in liquid CO₂ cannot be detected below 10 ppm by weight by using this near-ir band. The residual band at 1882 nm is due to CO₂, and any effect of drying CO₂ with P₂O₅ is impossible to monitor spectrophotometrically. Although no satisfactory means of monitoring H₂O in 0.1- to 1.0-ppm concentrations have emerged from this work, no adverse effects were observed which could be attributed to this level of contamination. Dilute I₂ solutions in P₂O₅-dried CO₂ were indefinitely stable, whereas with 10 ppm added H₂O considerable I₂ loss occurred. It was therefore presumed that the water concentration in dry CO₂ was no greater than 1 ppm and, at this level, would not interfere with the further aspects of the study.

Distribution Coefficients

The original KALC process assumed that I_2 would be deposited onto sorption beds before the CO_2 was liquefied. However, throughout the process there will be small amounts of I_2 escaping through the beds into the KALC system, and the distribution of such I_2 in the liquid and vapor phases of CO_2 will determine the amount of I_2 that is subject to follow the krypton or to be retained in the CO_2 . More recent thoughts include removing the total I_2 after liquefying the CO_2 by liquid-phase sorption techniques. With either philosophy of operation, the distribution coefficients for I_2 in the liquid and vapor phases of CO_2 are desirable.

Table 2 and Fig. 3 show these distribution coefficients for I_2 in CO_2 :

$$D = \frac{\text{mole fraction of } I_2 \text{ in } CO_2 \text{ liquid}}{\text{mole fraction of } I_2 \text{ in } CO_2 \text{ vapor}} = \frac{\text{absorbance of } I_2 \text{ in liquid}}{\text{absorbance of } I_2 \text{ in vapor}} \times \frac{\rho_v}{\rho_l},$$

Fig. 3. Distribution coefficients D for I_2 vs degrees kelvin.

Table 2. Distribution coefficients for 0.03 wt % I₂ in CO₂ as defined by the equation in text

Temperature		CO ₂ density (g/cc)		Distribution coefficient D	Method ^a
(°C)	(K ⁻¹ × 10 ³)	Liquid	Vapor		
30	3.30	0.593	0.340	2.46	1
25	3.36	0.714	0.242	5.42	1
19.2	3.42	0.786	0.188	9.17	1
14.7	3.48	0.827	0.159	14.2	1
14.0	3.48	0.834	0.155	14.9	1
10.0	3.53	0.864	0.135	29.7	1
9.9	3.53	0.865	0.134	24.7	1
5.0	3.60	0.898	0.114	53.6	1
0.8	3.65	0.924	0.099	77.5	1
0	3.66	0.929	0.096	74.9	1
0	3.66	0.929	0.096	92.4	1
-10	3.80	0.982	0.070	138	1
-10	3.80	0.982	0.070	122	2
-20.5	3.96	1.030	0.050	256	2
-26.0	4.05	1.055	0.042	348	2

^aMethod 1 = direct method; 2 = distillation method (see discussion in text).

where the peak absorbance² of I₂ was measured in the visible region at approximately 520 nm, and ρ is the density of CO₂ liquid (l) or vapor (v).

The great departure of CO₂ from ideality at pressures greater than 200 psia requires that an empirical gas equation be used for accurate determination of densities and/or molar volumes. The Beattie-Bridgeman equation¹¹ was selected for this purpose and is shown plotted for various temperatures in Fig. 4. The limited solubility of I₂ in liquid CO₂¹² plus the small amount of I₂ in the vapor precluded direct measurement of the D values at temperatures less than 0°C. Therefore a distillation method was adopted whereby vapors from a CO₂ solution saturated with I₂ at a fixed temperature were condensed in the spectrophotometer cell and then the I₂ concentration in the condensate was measured. This value

Fig. 4. Carbon dioxide molar density from Beattie-Bridgeman equation, compared with ideal gas.

represented the I_2 concentration in the equilibrated vapor, but enhanced by the ratio of the CO_2 liquid/vapor density for that temperature. In addition to the results shown in Table 1 for solutions of 0.03 wt % I_2 in liquid CO_2 , distribution coefficients at 20°C were measured for other I_2 concentrations (from 0.002 wt % to saturation with I_2) and were found to be identical to those in the table. These results suggest, therefore, that the much lower concentrations of I_2 in CO_2 expected in a KALC process would distribute between the phases in a similar fashion.

Since the partial pressure of I_2 is directly proportional to the I_2 mole fraction in the vapor, the distribution coefficients are proportional to the Henry's law constants expressed in atmospheres. (The proportionality constant is merely $\rho RT/44$, where ρ is the CO_2 vapor density at temperature T , 44 is the molecular weight of CO_2 , and R is the gas constant.) The constant value of D for CO_2 solutions varying from 0.002 to 0.179 wt % I_2 (saturation) therefore demonstrates the validity of Henry's law for this concentration range. Furthermore, the Henry's law behavior in this region leads us to anticipate the same behavior in much more dilute solutions, which is another way of stating the same conclusion reached in the preceding paragraph.

The distribution coefficients for CH_3I (0.02 to 0.1 wt % in CO_2) are given in Table 3 and Fig. 5. On comparing the I_2 data with these, it can be seen that above 0°C the slope of the line for CH_3I is much less than that for I_2 , whereas below 0°C it is comparable. Because CH_3I showed no solubility limits for the concentrations studied, it was possible to measure D values at lower temperatures than were measured for I_2 by merely increasing the concentration of CH_3I to the point where a measurable amount was present in the vapor. It was not necessary, therefore, to employ the distillation method used for the I_2 measurements.

Table 3. Distribution coefficients for 0.02 to 0.1 wt % CH_3I in CO_2

Temperature		Distribution coefficient D
($^\circ\text{C}$)	($\text{K}^{-1} \times 10^3$)	
27	3.34	3.45
25	3.36	3.65
21	3.40	3.58
15	3.47	5.87
15	3.47	6.70
10	3.53	8.20
10	3.53	9.80
5	3.60	10.80
0	3.66	14.70
-5	3.73	18.50
-10	3.80	22.50
-15	3.88	30.0
-15	3.88	32.5
-20	3.95	40.0
-25	4.03	46
-28	4.09	59
-30	4.11	59

Fig. 5. Distribution coefficients D for CH_3I vs degrees kelvin.

Corrosion Study

As stated earlier, I_2 in dry liquid CO_2 was stable. However, the addition of 3 ppm (or more) H_2O produced a corrosion reaction in the stainless steel vessel which caused the loss of I_2 and H_2O , formation of an insoluble product, and considerable etching of the metal surfaces. No corrosion reaction was observed for CH_3I from -30 to $+30^{\circ}\text{C}$, even in the presence of 500 ppm added H_2O . Methyl iodide invariably produced stable solutions in CO_2 , whether or not water was present. As a result of these observations, a series of corrosion experiments were initiated

for the I_2 solutions to determine the nature of the water interaction (reaction stoichiometry, etc.), to measure the reaction rates under various conditions, and to identify the products of the reaction. Some noteworthy observations have been made, even though a detailed corrosion mechanism cannot be presented.

The experiments were initially performed at 0°C with the intent of going to the more practical lower temperatures, but an I_2 mass transport process¹³ was encountered in the spectrophotometer cell which made it useless to pursue subzero temperatures in the present system. Therefore, the corrosion was examined at 21°C (ambient) instead, to eliminate the mass transfer problem. The corrosion behavior of I_2 at 0° was basically different from that at 21° , and consequently the two will be discussed separately.

At 0°C the I_2 loss followed a linear first-order reaction rate as shown in Fig. 6. The corrosion of the cell was typically greatest at the same place where the mass-transported I_2 formerly appeared in a dry

Fig. 6. Iodine loss in liquid CO_2 at 0°C for varying amounts of added H_2O .

CO₂ system (at the gas-liquid interface). The first-order plot and the region of corrosion attack led us to conclude that the rate was determined at 0°C by the first-order transport process. In addition, we found the mole ratio of water to I₂ consumed in the reaction at 0°C was typically in the range of 2 to 3. Evidence for the corrosion product was twofold: First, a solid crystalline product was isolated which was hygroscopic. X-ray fluorescence analysis of this material revealed iron and iodine as major, and chromium and nickel as minor constituents; but no successful match of diffraction lines from this product could be made with standard x-ray data. Second, an absorption band at 250 nm (see Fig. 7), which was unrelated to the reactants or to I⁻, grew in with the progress of the corrosion. This band might be due to a slight solubility of the crystalline product mentioned above, but this explanation is not yet certain.

Fig. 7. Absorption spectrum of the soluble corrosion product resulting from the reaction of I₂ and H₂O with the stainless steel vessel.

At 21°C the I_2 loss did not follow a linear first-order plot, but instead followed the unusual curves shown in Fig. 8. Typically, on release of water into a thoroughly equilibrated CO_2 solution of I_2 , the I_2 concentration showed a constant (or sometimes increasing) behavior prior to decreasing in a gradual, nonlinear fashion. For low concentrations of H_2O , the I_2 loss stopped (see curves A, B, and C, where the normalized concentration remained at 0.59, 0.14, and 0.02 approximately 100 hr later), even though some water was still indicated in the system. (These results suggest that an equilibrium might be reached.) The mole ratio of reacted H_2O to I_2 at 21°C was typically 1.0. The region of greatest corrosion attack was at the bottom of the cell around the point of water release and was generally greater in the liquid than at the gas-liquid interface. The solid corrosion product and the 250-nm band both appeared to be very similar to those of the 0°C run.

Fig. 8. Iodine loss in liquid CO_2 at 21°C for varying amounts of added H_2O .

In conclusion, it is believed that the 21°C corrosion reaction best represents that which would be expected for subzero dilute CO₂ solutions of I₂, which would experience no mass transport. Most of the corrosion product would be insoluble and in a static system would collect on the vessel walls. After a finite amount of H₂O had been consumed, the corrosion would subside, leaving the remaining I₂ in solution. The kinetics of this reaction and the products thereof cannot yet be described, because a thorough study of the reaction would exceed the limitations of the system and the time available. Since the reaction involves both I₂ and H₂O as reagents, a simplified approach such as the one used to obtain the data in Figs. 7 and 8 is inadequate. A more meaningful approach to the kinetic mechanism and rate would necessarily involve fixing either of the reactant concentrations to determine the order of the reaction for the other component.

Novel Species

Various reaction products and/or molecular combinations have been considered in the CO₂-I₂-H₂O-stainless steel quaternary system. The only reaction products found in this system have been from the impurity reaction of I₂ with organic components and the corrosion reaction of I₂ and H₂O with stainless steel. Both of these have already been discussed in the previous paragraphs and will not be treated here.

Instead, attention was directed at the possibility of novel molecular combinations of CO₂, I₂, and H₂O which could control the distribution of H₂O and I₂ in the CO₂ system. Several such combinations (or species) were considered in detail.

CO₂-I₂

The first involved a species which might be formed by the direct combination of I₂ and CO₂. Previous authors⁸ isolated a low-boiling product which they suggested was such a CO₂-I₂ species. However, our experiments in a clean system have not substantiated their observations. We have concluded that no CO₂-I₂ phase exists and that the previously

proposed low-boiling species was, instead, the product of I_2 and the organic impurities.

Nevertheless, association of I_2 and CO_2 is observed in the CO_2 phases. It is evident in the vapor because at $0^\circ C$ approximately three times more I_2 is found than would be anticipated from the I_2 vapor pressure alone. It is evident, also, in the liquid because the I_2 absorption band shifts due to ordinary solvation effects. But this association, as stated above, only determines the distribution of I_2 between the two phases and is not great enough to result in the formation of a separate phase.

$CO_2 \cdot H_2O$

The second possible association which might occur is that between CO_2 and H_2O . Although it is recognized to occur in condensed phases, no evidence to date has been reported for the association in the vapor.¹⁴ The spectra in Fig. 9 establish the formation of a $CO_2 \cdot H_2O$ vapor species

Fig. 9. Vapor spectra at $25^\circ C$ in 34.42-cm-pathlength CO_2 cell.

by the bands at 1380 and 1880 nm, which occur when water and CO₂ are together in the system. The similarity of these bands to those of a free water molecule suggests that, although association occurs to increase the amount of H₂O in the vapor phase, it is not great enough to distort the fundamental vibrational modes of water.

The CO₂·H₂O data have been interpreted by assuming that the following equilibrium is established in the vapor phase:

The net increase in absorbance at 1880 nm with increasing CO₂ pressure was assumed to be due solely to the (CO₂)_n·H₂O species and to CO₂. By subtracting the CO₂ contribution, the absorbance of the association species could be determined. A logarithmic plot of species concentration vs CO₂ concentration should be linear, with a slope equivalent to n if a single species is formed. However, the plots in Fig. 10 show curves with slopes varying from 0 to 2, suggesting that n varies between these limits as a function of CO₂ pressure.

Widom and Bauer¹⁴ have considered the interaction of CO₂ and H₂O from the standpoint of energy exchange in molecular collisions and have determined that the most favorable orientation for a collision is one leading to the formation of a CO₃²⁻ ion. They estimate that the interaction potential is of the order of 8 kcal/mole. Nevertheless, they recognize that H₂O and CO₂ do not produce a stable product in the gas phase. Our data clearly establish the CO₂·H₂O product in the presence of very high CO₂ pressures, which, along with the characteristic H₂O vibrations, confirm the weakness of the interaction. Evidence for the appearance of CO₃²⁻ vibrations was not found, suggesting further that the interaction forces between the two molecules are very weak indeed.

Fig. 10. Water-carbon dioxide association product concentration vs CO_2 concentration for the vapor phase reaction of CO_2 and H_2O as determined by the 1880-nm band.

I₂-I₂

Finally, some evidence for the formation of an I₄ species previously reported in CCl₄ solutions⁵ has been observed by us¹⁵ in CCl₂F₂ (Freon-12) solutions. Examination of I₂ in CO₂ at high concentrations suggests a trace of I₄ by the appearance of a very weak band at 260 nm. The concentration of I₄ in CO₂ is, however, 10 to 100 times less than that found in CCl₂F₂, presumably because the equilibrium $2I_2 \rightleftharpoons I_4$ is shifted to the left by the stronger solvation forces of CO₂. Although the I₄ concentration cannot be accurately determined because of uncertainties⁵ in the molar extinction coefficient² for I₄, the I₄/I₂ ratio in CO₂ is estimated to be less than 10⁻³.

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REFERENCES AND FOOTNOTES

1. KALC = krypton absorption in liquid carbon dioxide method of separating krypton from CO₂ in high-temperature gas-cooled reactor fuel reprocessing.
2. Absorbance (A) as defined by Beer's law, $A = \epsilon c l$, where ϵ is the molar extinction coefficient in liters mole⁻¹ cm⁻¹, c is the concentration in moles/liter, and l is the pathlength in cm.
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6. This notation for overtone and combination bands for a particular vibration is as follows: (0,1,2) = ($\nu_1\nu_2\nu_3$), that is, none of the first, one of the second, and two quanta of the third vibration have been excited to give rise to this transition.
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