



Research paper

I₂O in solution and volatilityStanley D. Furrow^a, Guy E. Schmitz^{b,*}^a Penn State Berks College, The Pennsylvania State University, Reading, PA 19610, United States^b Université Libre de Bruxelles, Faculty of Applied Sciences, CP165/63, Av. F. Roosevelt 50, 1050 Brussels, Belgium

HIGHLIGHTS

- I₂O can be prepared in 96% sulfuric acid and extracted in chlorinated solvents.
- UV–vis spectra are presented in DCM and CCl₄.
- These solutions offer new methods for studies of the I(+1) properties.
- I₂O forms an ionic complex in acetonitrile preserving the I(+1) oxidation state.
- I₂O is a volatile compound with consequences in atmospheric chemistry.

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ABSTRACT

I(+1) formed by reacting iodine with KIO₃ in 96% sulfuric acid is partly in the form of I₂O that can be extracted in dichloromethane (DCM). The extraction process is an interesting coupling between phase transfer and chemical reactions allowing to obtain solutions containing nearly no iodine. I₂O solutions can also be obtained in other chlorinated solvents and forms probably an ionic complex in acetonitrile. UV–vis spectra are presented (ϵ (I₂O, 442 nm) = 259 in DCM). Distillations of I₂O solutions and gas phase diffusion at laboratory temperature show that I₂O is a volatile compound that should be considered in atmospheric chemistry.

1. Introduction

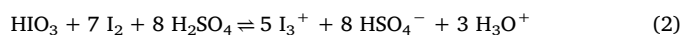
Muntean et al. [1] proposed a new method for preparing I(+1) by reacting iodine with KIO₃ in 96% sulfuric acid. They showed that the I(+1) formed can be extracted into DCM and assumed that I(+1) was in the form of I₂O. The existence of I₂O, had already been proposed in 1987 [2] as an intermediate in a model of the Bray-Liebhafsky oscillating reaction. This model was completed and confirmed later [3,4] and it was shown that I₂O is at the heart of the destabilizing feedback [5,6]. I₂O was also proposed as an intermediate in a mechanism of the HOI disproportionation in acetic solutions [7,8]. However, there was no direct proof of its existence and I₂O is still mentioned in Wikipedia as “unknown”. A proof was obtained only recently [9] by a study of the solutions of I₂ and KIO₃ in 96% sulfuric acid over a very wide range of concentrations. These solutions contain I(+1) in the form of I₃⁺ and I₅⁺, already known in pure sulfuric acid [10–15], but all the experimental results can be explained only if I₂O is also formed.

After a summary of the main features of the I₂O solutions in 96% sulfuric acid, the section “Extraction of I₂O into DCM” shows that this extraction is not a simple physical phenomenon but an interesting

coupling between phase transfer and chemical reactions. This coupling makes it possible to obtain almost pure solutions of I₂O in DCM. The next section discusses the possibility of using other solvents and gives UV–vis spectra. The last section shows that I₂O is a volatile compound. Distillation of DCM containing I₂O extracted from H₂SO₄ gives a distillate containing also I₂O. Further evidence of this volatility in DCM is presented and I₂O can even be transferred directly from its solutions in 96% sulfuric acid to the gas phase.

2. I₂O in 96% H₂SO₄

The UV–vis spectra of I₂ and KIO₃ solutions in 96% sulfuric acid [9] with ratios between initial concentrations varying from [I₂]₀/[KIO₃]₀ = 1/3 to 8 and [I₂]₀ varying from 2.4 × 10^{−4} M to 1.2 × 10^{−2} M show that the composition of these solutions is described by the stoichiometric Eqs. (1)–(4).



* Corresponding author.

E-mail address: gschmitz@ulb.ac.be (G.E. Schmitz).<https://doi.org/10.1016/j.cplett.2019.05.052>

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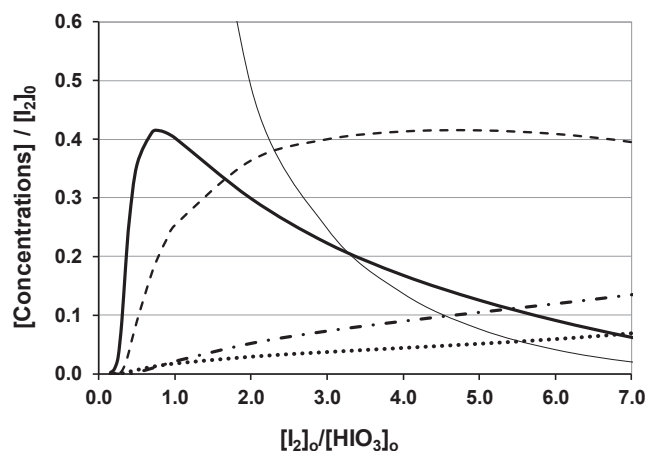
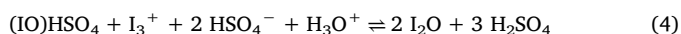


Fig. 1. Calculated concentrations if $[I_2]_0 = 1 \times 10^{-3}$ M. I_2O (—), $(IO)HSO_4$ (---), I_3^+ (- · - ·), I_5^+ (· · ·), I_2 (....).



Reactions (1)–(3) were previously known in 100% sulfuric acid [10–15] but are not sufficient to explain the results obtained in 96% sulfuric acid. In particular, the measurement of the I(+1) concentrations by the crotonic acid method [16,17] has shown that the total concentration of I(+1) passes through a maximum for ratios $[I_2]_0/[KIO_3]_0$ between 1 and 2, an observation that cannot be explained by reactions (1)–(3). After eliminating various forms of I(+1), such as $IHSO_4$, we concluded that this form can only be I_2O . The stoichiometric equation (2) $HIO_3 + 4 I_2 + H_2SO_4 = 5 I_2O + HSO_4^- + H_3O^+$, combination of (1), (2) and (4), gives a ratio $[I_2]_0/[KIO_3]_0 = 2$ for the I_2O formation. Experimentally, the maximum concentration of I_2O is obtained for a smaller ratio because of the reversibility of reactions (1)–(4). Fig. 1 shows an example of calculated equilibrium concentrations. The details of the calculations are explained in the electronic supplementary information of our previous paper [9]. The ratios $[Concentrations]/[I_2]_0$ do not vary much with $[I_2]_0$. The reversibility of reactions (1)–(4) also explains why Noszticzius et al. [18] observed that solutions of I(+3) containing a very small amount of I(+1) can only be obtained for ratios $[I_2]_0/[KIO_3]_0$ well below 1/3 suggested by reaction (1).

3. Extraction of I_2O into DCM

Solutions of I_2 and KIO_3 in 96% sulfuric acid with a ratio $[I_2]_0/[KIO_3]_0 < 2$ and an initial concentration $[I_2]_0 \sim 10^{-2}$ M are very dark. When DCM is added, it becomes purple, showing that iodine is extracted (Fig. 2 A). When stirring begins, both layers becomes very dark. After 30–40 min the sulfuric acid phase becomes less dark and the color of the DCM phase changes to orange-brown (Fig. 2B and C). On further stirring, the sulfuric acid is completely discolored (Fig. 2D). This evolution is too slow for a simple extraction process and the rate of the whole process is limited by chemical reactions. It is explained adding reactions (5) and (6) to the reactions (1)–(4). For simplicity, the concentrations in the sulfuric acid phase are noted without subscript.



The sulfuric acid contains some iodine which is quickly extracted explaining the initial color of the DCM phase. However, the extraction of I_2O shifts reaction (4) to the right and, consequently, also reactions (1) and (2) to the right. Iodine in the sulfuric acid is consumed and iodine in the DCM phase goes back to the sulfuric acid. If there is initially an excess of iodate, this process continues until nearly all the

iodine has reacted. The displacements of the reactions (1)–(6) are linked and become slower as the I_2 concentration becomes smaller explaining the long time necessary to obtain a solution of I_2O in the DCM containing very little I_2 . Fig. 3 shows the initial spectrum of the sulfuric acid phase and the final spectra of both phases. The high absorbance of the initial sulfuric acid at short wavelengths corresponds to $(IO)HSO_4$ and the two peaks at 290 and 455 nm to I_3^+ and I_5^+ . After the extraction, the absorbance at short wavelengths is much lower leaving only the contribution of the excess of iodate and the peaks at 290 and 455 nm have disappeared. Thus, $(IO)HSO_4$, I_3^+ and I_5^+ were consumed. The spectrum of the DCM phase is the spectrum of I_2O discussed in the next section.

As a further test of the purity of the I_2O solutions in DCM, we analyzed its sulphate content using the barium method explained in the experimental section. These tests revealed no measurable amount of sulphate. An improved recipe for the preparation of I_2O solutions in DCM is also given in the experimental section. These solutions are stable more than one month.

The final solution of I_2O in DCM contains almost no iodine proving that the equilibrium constant K_5 is sufficiently large to shift reaction (4) nearly completely to the right. According to the global reaction $2 HIO_3 + 4 I_2 + H_2SO_4 = 5 I_2O$ (in DCM) + $HSO_4^- + H_3O^+$, the final amount of I_2O in the DCM approaches 5/4 the amount of I_2 used to prepare the solutions. This is much more than the amount in the sulfuric acid before the extraction. Numerical simulations of this coupling extraction - reactions are presented in the electronic supplementary information. They confirm the above discussion and allow to simulate the effect of the experimental conditions.

4. Spectra of I_2O in different solvents

The maximum absorbance of I_2O in DCM is observed at 442 nm with a molar absorption coefficient $\epsilon(I_2O, 442 \text{ nm})$ measured as follows. When a small amount of a solution of I_2O in DCM is added to a large amount of acidified water, I_2O is quickly hydrolyzed into HOI, the amount of which was measured using two methods giving nearly the same results. The first method is classical iodometry. A sample of I_2O in DCM is added to an acidic solution containing an excess of iodide and the produced iodine ($I_2O + 2H^+ + 2I^- \rightarrow 2I_2 + H_2O$) is titrated with $Na_2S_2O_3$. The average of five measurements gave $\epsilon(I_2O, 442 \text{ nm}) = 261$. If a small amount of I_2 is present initially in the I_2O solution, it is included in the result of the $Na_2S_2O_3$ titration. The second method uses the reaction of I(+1) with crotonic acid (CA) [16,17] producing an iodohydrin in dilute $HClO_4$: $HOI + CA \rightarrow HOICA$ or $I_2O + H_2O + 2CA \rightarrow 2HOICA$. A sample of I_2O in DCM is injected in an acidic solution of CA and the amount of HOICA produced is calculated from the absorbance at 278 nm ($\epsilon(HOICA, 278 \text{ nm}) = 379$) corrected for the unreacted CA ($\epsilon(CA, 278 \text{ nm}) = 3.73$). The average of seven measurements gave $\epsilon(I_2O, 442 \text{ nm}) = 257$. Iodine reacts very slowly with CA so that iodine does not affect these measurements. Moreover, after the CA reaction, iodine shows a peak at 461 nm ($\epsilon(I_2, 461 \text{ nm}) = 746$) allowing to calculate its concentration. These experiments gave a ratio $[I_2]/[I_2O]$ in the DCM usually $< 1\%$.

I_2O solutions in DCM provide new methods for studying the properties of I(+1) compounds. In particular, the kinetics of the disproportionation of HOI [7,8] is still not well known, deserves further study and we have made some preliminary measurements. When a sample of I_2O in DCM is added to diluted $HClO_4$, the fast hydrolysis reaction $I_2O + H_2O \rightleftharpoons 2HOI$ is followed by the slow reaction $5HOI \rightarrow IO_3^- + H^+ + 2I_2 + 2H_2O$. The iodine produced after one or two days was measured by absorptiometry. According to these reactions, 5 mol of I_2O give 4 mol of I_2 and the concentration of I_2O in the initial solution can be calculated. The ratios between the measured absorbances of the I_2O solutions and their concentrations calculated with this method give an average value $\epsilon(I_2O, 442 \text{ nm}) = 258$ for six experiments with $[HClO_4] = 0.03$ to 0.10 M. The excellent agreement between three

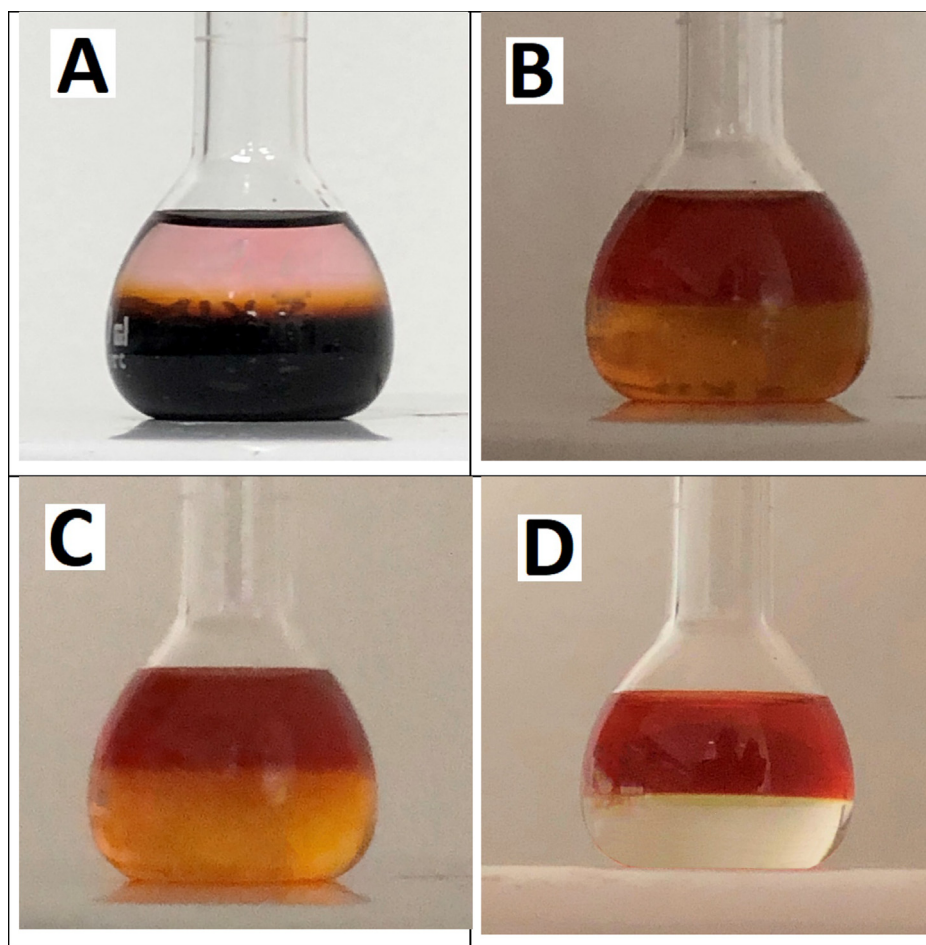


Fig. 2. Extraction of I_2O into DCM in the upper layer; 96% H_2SO_4 with $[I_2]_0/[KIO_3]_0 = 1.24$ in the lower layer. The mixture was continuously stirred except for taking the photos.

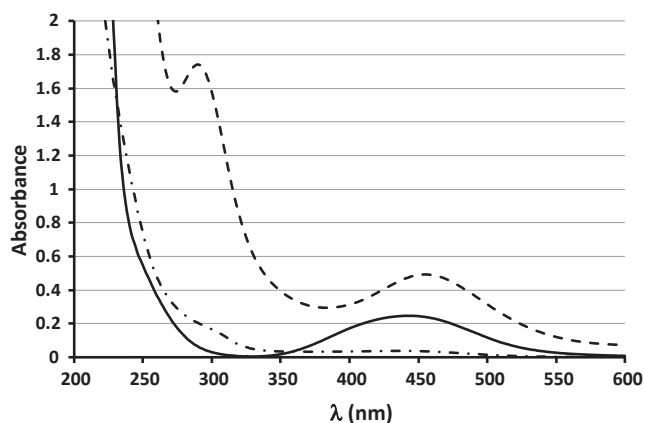


Fig. 3. Initial H_2SO_4 solution, $[I_2]_0/[KIO_3]_0 = 1.024$, $[I_2]_0 = 7.20 \times 10^{-3} M$ (— — —); Final H_2SO_4 solution (- · - ·); DCM layer (—).

different types of ϵ measurements confirms the above reactions.

The spectrum of I_2O in DCM is shown in Fig. 4 with the spectrum of I_2 . I_2 shows a maximum at 505 nm with $\epsilon(I_2, 505 \text{ nm}) = 911$ (average of six measurements). I_2O prepared in 96% sulfuric acid can also be extracted into $CHCl_3$ and CCl_4 and Fig. 4 shows its spectrum in CCl_4 for comparison with DCM. The maximum is at 458 nm, instead of 442 nm. The absorption coefficient is estimated, not measured. Fig. 4 shows also the spectrum of a mixture containing 90% of I_2O and 10% of I_2 . The concentration of I_2 in an I_2O solution is difficult to measure at 505 nm,

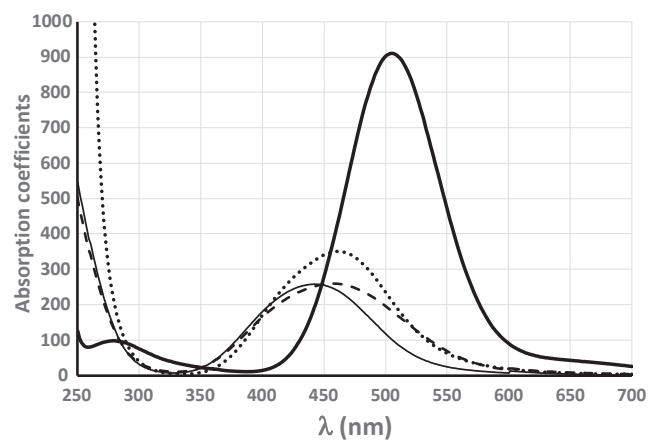


Fig. 4. Absorption coefficients. I_2 in DCM (—), I_2O in DCM (— — —), mixture 90% I_2O and 10% I_2 in DCM (- · - ·), I_2O in CCl_4 (....) estimated.

but a good approximation can easily be obtained by measuring the shift of the peak at 442 nm towards longer wavelengths. For more precise measurements, the method with CA mentioned above can be used.

The preparation of HOI solutions by hydrolysis of I_2O dissolved in DCM has the drawback of the low solubility of DCM in water (about 15 g/L at 20°) and we have looked for other solvents. However, I_2O reacts with most of the usual solvents either as oxidizing agent or as iodizing agent. A special case is that of acetonitrile which could be interesting because acetonitrile is completely miscible with water.

Solutions of I_2O in acetonitrile cannot be obtained by extraction from concentrated sulfuric acid because they react violently, but they can be obtained by distillation of a mixture of acetonitrile (B.P. 80°) and I_2O in DCM (B.P. 40°). During this distillation, I_2O remains mainly in the acetonitrile. A recipe is given in the experimental section. I_2O dissolved in acetonitrile shows a peak at 354 nm and a very large absorbance increasing below 300 nm. The difference with DCM seems too large for a simple solvent effect. We have also observed that the conductance increases very markedly when I_2O is dissolved in acetonitrile while it changes little when about the same amount is dissolved in DCM. I_2O probably forms an ionic complex in acetonitrile similar to that formed by I_2 . I_2 dissolved in acetonitrile gives a peak at 462 nm but also two peaks slowly increasing at 290 and 364 nm. They are explained by the complexation reaction $CH_3CN + 2 I_2 \rightleftharpoons CH_3CNI^+ + I_3^-$ [19,20]. As a further test, we have diluted a solution of I_2O in acetonitrile with a 0.1 M solution of $HClO_4$ and followed the disproportionation of HOI produced by hydrolysis. The time evolution was similar to that observed with DCM but the rate was lower. We conclude to a reversible complexation reaction conserving the $I(+1)$ oxidation state.

5. I_2O is a volatile compound

One of us (S.F.) discovered that when distilling a solution of I_2O in DCM, he obtained a distillate containing I_2O . Fig. 5 gives an example of results. The distillate shows the same peak at 442 nm as the original solution showing that I_2O is a volatile compound. Fig. 5 shows also that the concentration of I_2O is smaller in the distillate than in the initial mixture and larger in the residue. I_2O is volatile but less than DCM. Similar results are obtained by distilling solutions of I_2O in CCl_4 . The three spectra have a maximum at 458 nm but their order is reversed. The concentration of I_2O is higher in the distillate than in the initial mixture showing that I_2O is more volatile than CCl_4 . The residue has the same spectrum as the initial solution, indicating that the solution of I_2O is stable at the boiling point of the CCl_4 ($76.7^\circ C$).

Volatility of I_2O was confirmed by very simple experiments at room temperatures using a flask with a side arm represented in Fig. 6. When an I_2O solution is placed in the side arm and pure DCM or CCl_4 in the bottom of the flask, I_2O diffuses slowly in the gas phase and its concentration increases in the DCM or CCl_4 . The most outstanding result of these experiments was obtained by placing CCl_4 in the bottom of the flask and a solution of $I(+1)$ in 96% sulfuric acid ($[I_2]_0/[KIO_3]_0 < 2$) in the side arm. The bottom of the flask was in cold water ($5\text{--}10^\circ C$ below the room temperature) and the side arm was slightly heated (a few degrees above the room temperature). Within 20 min, the CCl_4 was yellowish. The shape of its spectrum was identical to the above spectra of I_2O in CCl_4 . This is a simple and direct proof that not only DCM but also the sulfuric acid solutions contain volatile I_2O .

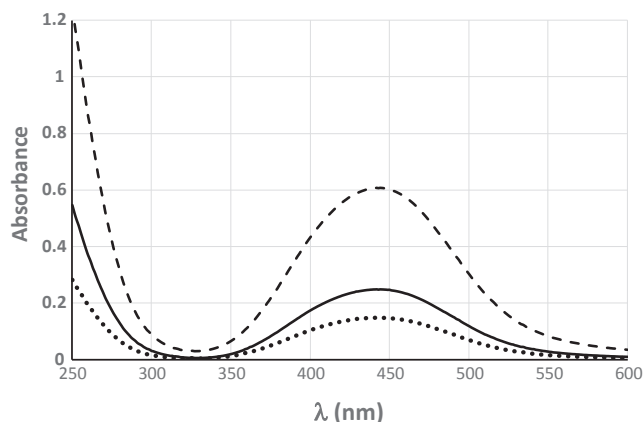


Fig. 5. Distillation of a solution of I_2O solution 9.6×10^{-3} M in DCM. Initial solution, (—), distillate (•••), residue (---).

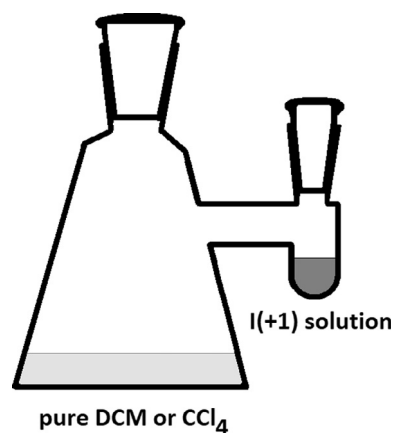


Fig. 6. Side arm flask used to show the volatility of I_2O above DCM, CCl_4 and 96% H_2SO_4 .

We also obtained the gas-phase I_2O spectrum by pouring a small layer of I_2O in DCM in a spectrophotometer cell and heating the cell in a sand bath at about $60^\circ C$. DCM being more volatile than I_2O , the solution becomes more concentrated. Just before all the DCM has evaporated, the cell is transferred to the spectrophotometer. Fig. 7 shows the spectrum obtained by passing the light beam through the gas phase. The $I_2O(g)$ peak at 243 nm is not observed in solution because DCM strongly absorbs at this wavelength. The peak at 469 nm is a little shifted compared with the peak at 442 nm of I_2O in DCM. DCM does not absorb at 469 nm and iodine vapor would give a peak at 526 nm.

The stability of $I_2O(g)$ that we observed is consistent with earlier theoretical estimates of its thermodynamic properties. I. Novak [21] obtained $\Delta_f H_{298} = 121.9 \text{ kJ mol}^{-1}$ for $I_2O(g)$ and concluded that it can be sufficiently stable for detection and synthesis. Values calculated later [22–25] are between 92.4 and $111.2 \text{ kJ mol}^{-1}$. With $S_{298} = 306.5 \text{ J K}^{-1} \text{ mol}^{-1}$ [22], we obtain estimates of the equilibrium constant of the reaction $2 HOI(g) = I_2O(g) + H_2O(g)$ between 10^{-3} and 1. The formation of $I_2O(g)$ is therefore possible in a dry atmosphere. It can also be formed in the troposphere by the reaction $IO' + I' + M \rightarrow I_2O + M$ and by reactions of iodine derivatives with ozone [26].

6. Conclusion

It may seem surprising that a new simple compound of iodine has been isolated only recently. This has two reasons. The first is that the concentration range of sulfuric acid for preparing I_2O is narrow. It is not

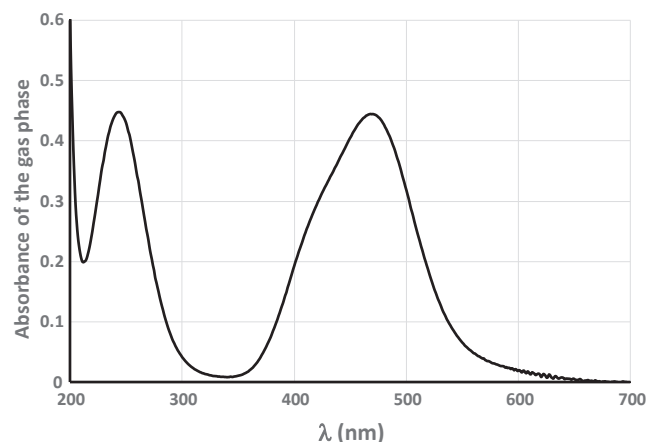


Fig. 7. Spectrum of the gas phase obtained by evaporation of an I_2O solution in DCM.

formed in pure acid because the concentrations of HSO_4^- and H_3O^+ are very small so that the equilibrium of reaction (4) is shifted to the left. It also does not form in acid not concentrated enough because I_2O is stable only in anhydrous media. The second reason is that I_2O is very reactive and we have only obtained stable pure solutions in chlorinated solvents. These solutions suggest new methods of studying the properties of $\text{I}(+1)$ and further kinetic studies in solutions. Another important result is the volatility of I_2O . I_2O is a possible intermediate in atmospheric chemistry [27,28] not mentioned in recent models and our results paves the way for studies of its gas phase properties.

7. Experimental

The experimental methods have been described previously [1,9] and some information is given in the text. Only particular recipes used in this work are given here.

7.1. Barium analysis of sulfates in the DCM solutions

A solution of 0.022 M I_2 and 0.0099 M KIO_3 in 20 ml H_2SO_4 and 8 ml DCM was stirred for two days. The DCM layer was separated and distilled. 5 ml of the distillate was added to an acidic solution of barium nitrate and potassium iodide (to react with I_2O), stirred until the DCM layer was much lighter, then heated to near boiling, then let stand for two days. The solution was clear, showing no barium sulfate.

7.2. New recipe for the preparation of a solution of I_2O in DCM

Weighed amounts of I_2 and KIO_3 with ratio $[\text{I}_2]_0/[\text{KIO}_3]_0 < 2$ and $[\text{I}_2]_0 \sim 10^{-2}$ M. are stirred during about one day with a weighed amount of 96% H_2SO_4 . Add an equal volume of DCM to this solution, stir vigorously for approximately 3 h, then separate the layers. Distill the majority of the DCM layer at 50 to 70 °C to a flask cooled in ice water. Alternatively, the DCM may be added initially to directly prepare I_2O in DCM. The reaction is faster, but we recommend stirring the mixture during about one day.

7.3. Preparation of a solution of I_2O in acetonitrile

Prepare I_2O the usual way by dissolving solid I_2 and KIO_3 in concentrated H_2SO_4 and DCM. When the H_2SO_4 layer becomes light and the DCM layer dark, perform a simple distillation at ~50–70 °C. The I_2O is mainly carried over to the distillate. Next add a few ml of acetonitrile to the DCM distillate. **WARNING:** do not let acetonitrile come in contact with concentrated H_2SO_4 because they react violently. Do another simple distillation heating to ~70 to 75 °C until the process slows down appreciably. This time the distillate, mainly DCM, is clear. The I_2O remains in the residue, mainly acetonitrile (B.P 81.7 °C). The separation of DCM is not complete and some remains in the residue. However, 0.10 ml of the residue with I_2O dissolves in 4 ml water with just a few seconds shaking.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2019.05.052>.

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