and normal $KHSO_5$. Both the H_2O_2 used in preparing the labeled Caro's acid and the H_2O_2 obtained by acid hydrolysis of the $KHSO_5$ sample had the same amount of double labeling within experimental error. Therefore it is certain that the sample of $KHSO_5$ to be used in the decomposition runs was properly labeled (*i.e.*, no scrambling occurred during preparation) and that no peroxide oxygen exchange with solvent water occurs.

The data for three decomposition experiments (CO_3^{2-} I, CO_3^{2-} II, and HPO_4^{2-} are their symbols in Table I) are presented in Table I along with the comparative data for the H_2O_2 samples mentioned above. All data are given for the same mass spectrometer settings, and all of the decomposition solutions contained sufficient EDTA to eliminate trace metal catalysis; comparative kinetic runs with the same buffer solutions showed second-order kinetics as expected.[1-4] The first two samples were from decomposition runs carried out in carbonate at the pH of maximum decomposition rate[1]; the third sample, from a phosphate buffer, showed the expected lower rate but give otherwise identical results.

The data of Table I show, in the third column, the total atom per cent O^{18} in our samples of oxygen gas both from Caro's acid decomposition and from hydrogen peroxide. Since the values are the same within experimental error, exchange with solvent water either before, during, or after the decomposition is excluded. Since the value for O_2^{36} per cent is the same (see fourth line) both before formation of $KHSO_5$ and after hydrolysis, no scrambling occurs in the preparation of the sample to be decomposed.

TABLE I

ISOTOPE TRACER RESULTS FOR CARO'S ACID DECOMPOSITION

Sample	pH	Atom % O^{18}	O_2^{36}, %
CO_3^{-2} I[a]	9.4	1.42 ± 0.01	0.09 ± 0.02
CO_3^{-2} II	9.4	1.38	0.12
PO_4^{2-}[a]	7.4	1.44 ± 0.01	0.10 ± 0.02
H_2O_2[b]	...	1.44 ± 0.05	1.08 ± 0.02

[a] Average of two mass spectrometer runs. [b] Average of four samples (eight mass spectrometer runs): two samples by ceric ion oxidation of H_2O_2 used in preparation of Caro's acid and two samples obtained by hydrolysis of Caro's acid followed by ceric ion oxidation. The validity of such check experiments has been previously demonstrated: C. A. Bunton and D. R. Llewellyn, *Research*, **5**, 142 (1952); M. Anbar, *J. Am. Chem. Soc.*, **83**, 2031 (1961).

If complete scrambling during decomposition had occurred, the values for O_2^{36} per cent for the first three entries in the column would be $\sim 0.02\%$. If no scrambling had occurred, the values would be $1.08 \pm 0.02\%$ as observed for the hydrogen peroxide samples. The data of Table I show that the oxygen molecules which result from spontaneous decomposition of Caro's acid are predominantly ($91 \pm 2\%$), but not completely, scrambled. Therefore any mechanism such as II is eliminated by the results. The isotope tracer results obtained here are consistent with nucleophilic displacement on oxygen by oxygen; indeed our data are direct evidence that such a displacement can occur.

The observation that small amounts of peroxydisulfate ion[3] and hydrogen peroxide[5] are formed during the decomposition of HSO_5^- suggests that peroxide metathesis

$$2HSO_5^- \rightarrow S_2O_8^{2-} + H_2O_2$$

can occur to a small extent during the decomposition.

Depending on the nature of the peroxide, decomposition *via* displacement on oxygen by oxygen (as appears to be the predominant situation here) or decomposition *via* attack at some other electrophilic center (as in the case of the peroxyacetic acid decomposition[4]) may occur. Since in neither case did we observe 100% compliance with the predicted isotope distribution for a single mechanistic path, it seems reasonable to conclude that peroxide decompositions of this type involve two competing pathways having identical rate laws. For example, the fact that 9% of the activated complexes (over and above the statistical probability) led to doubly-labeled oxygen molecules in this study can be interpreted as being due to a small contribution of an activated complex involving peroxy anion attack on sulfur (mechanism II). We hope to be able to sort out the relative rates for these competing paths in the future.

Experimental

The mixture of double-labeled H_2O_2 and normal H_2O_2 was prepared as in the previous study.[4] The preparation of Caro's acid followed the procedure of Ball[1]; solid $KHSO_5$ was made from the acid by careful neutralization with $KHCO_3$ and rapid evaporation of water.[3] Other procedures followed those employed previously.[1,4]

In the initial step of the synthesis (reaction of double-labeled oxygen with metallic sodium), a small amount of oxygen exchange with the glass vessel apparently took place for we found some $H_2O^{16}O^{18}$ in our hydrogen peroxide samples. This did not affect our results, since it only involved a small and constant correction factor for each experiment.

Acknowledgments.—We wish to thank Dr. K. M. Ibne-Rasa for suggestions, Dr. G. O. Dudek of Harvard University for aid with the mass spectrometer, and the U. S. Atomic Energy Commission for financial aid.

(5) G. Levey, unpublished results.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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Dimethyl(trifluoromethylthio)arsine and Related Compounds[1]

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It has recently been reported[2] that bis(trifluoromethyl) disulfide reacts with tetrafluorohydrazine on

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(1) This work was supported by the National Research Council of Canada.

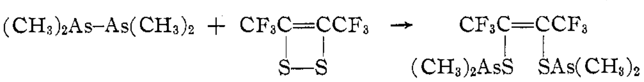
(2) E. C. Stump and C. D. Padgett, *Inorg. Chem.*, **3**, 610 (1964).

ultraviolet irradiation to give trifluoromethylthiodifluoramine. We wish to report some analogous reactions of compounds containing As–As and S–S bonds.

Tetramethyldiarsine and bis(trifluoromethyl) disulfide react at 20° to give dimethyl(trifluoromethylthio)arsine, b.p. 115°, in good yield.

$$(CH_3)_2As{-}As(CH_3)_2 + CF_3S{-}SCF_3 \rightarrow 2(CH_3)_2AsSCF_3$$

The identity of the new compound is confirmed by its synthesis from chlorodimethylarsine and bis(trifluoromethylthio)mercury. The S–S bond of bis(trifluoromethyl)-1,2-dithietene is also readily cleaved by tetramethyldiarsine yielding 1,4-bis(dimethylarsino)2,3-bis(trifluoromethyl)1,4-dithiobut-2-ene, an air-sensitive, pale red liquid, b.p. 92–95° (10^{-3} mm.). The infrared spectrum of the product shows a strong C=C band at 1535 cm.$^{-1}$, indicating the expected *cis* configuration. Krespan and McKusick[3] report a similar frequency, 1540 cm.$^{-1}$, for the *cis* isomer of $CF_3(CH_3S)C{=}C(SCH_3)CF_3$.



$$(CH_3)_2As{-}As(CH_3)_2 + \underset{S{-}S}{CF_3C{=}CCF_3} \rightarrow \underset{(CH_3)_2AsS\quad SAs(CH_3)_2}{CF_3C{=}CCF_3}$$

It has also been found that tetramethyldiarsine reacts with bis(trifluoromethyl) peroxide and with tetrafluorohydrazine, although in neither case was the expected product isolated at 20°.

Experimental[4]

Reaction of Tetramethyldiarsine with Bis(trifluoromethyl) Disulfide.—The diarsine (3.2 g.) and the disulfide (6.3 g.) were left for 7 days at 20°. No diarsine was left and distillation of the reaction mixture gave 5.0 g. of dimethyl(trifluoromethylthio)arsine, b.p. 115°. *Anal.* Calcd. for $C_3H_6AsF_3S$: As, 36.4; F, 27.7; S, 15.6. Found: As, 36.2; F, 27.9; S, 15.5. The n.m.r. spectrum showed a single proton signal at τ 8.40. Infrared spectrum (liquid film, main bands): 3000 (m), 2910 (m), 1415 (m), 1262 (m), 1223 (m), 1110 (broad, vs), 900 (m), 752 (m) cm.$^{-1}$.

Reaction of Tetramethyldiarsine with Bis(trifluoromethyl)1,2-dithietene.—The diarsine (6.4 g.) and the dithietene (7.2 g.) were left at 20° (2 days). Distillation at 10^{-3} mm. resulted in considerable decomposition; however, 3.0 g. of a pale red product was isolated which distilled in the range 92–95°. This was identified as 1,4-bis(dimethylarsino)2,3-bis(trifluoromethyl)1,4-dithiobut-2-ene. *Anal.* Calcd. for $C_8H_6As_2F_6S_2$: C, 22.1; H, 2.5; As, 34.4; F, 26.1; S, 14.7. Found: C, 22.2; H, 2.9; As, 34.2; F, 26.1; S, 14.6. The n.m.r. spectrum showed a single proton peak at τ 8.22. Infrared spectrum (liquid film, main bands): 1535 (m), 1416 (m), 1235 (br, vs), 1150 (br, vs), 890 (m), 836 (m), 716 (m), 677 (m), 655 (m) cm.$^{-1}$.

Reaction of Chlorodimethylarsine with Bis(trifluoromethylthio)mercury.—Chlorodimethylarsine and excess mercurial react at 20° (2 days) to give a nearly quantitative yield of dimethyl(trifluoromethylthio)arsine, identified by means of its boiling point of 115° and its infrared spectrum.

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(3) C. G. Krespan and B. C. McKusick, *J. Am. Chem. Soc.*, **83**, 3438 (1961).

(4) Reactions were done in sealed tubes. N.m.r. spectra were run on a Varian A60 instrument; neat liquid samples were used and peaks are reported relative to an external tetramethylsilane standard. Microanalyses were done by Dr. Alfred Bernhardt, Mulheim, Germany.

Correspondence

Concerning Recently Reported Values of the Association Constants of Silver Chloro Complexes in Fused Lithium Nitrate–Potassium Nitrate Eutectic

Sir:

As a result of some recently acquired information,[1] it has become apparent that an error in calculation was committed in our recent paper.[2] We should like to take this opportunity to correct the error and comment on the general method.

It is now experimentally apparent[1,3] that quasi-lattice type calculations are applicable to systems in which the sizes of the ions differ appreciably. When applied to the $Ag^+{-}Cl^-$ ion pair in $LiNO_3{-}KNO_3$ eutectic at 225°, the association constant reported in our paper seems much too high. Re-evaluating our work, it became apparent that an error was made in calculating the equilibrium concentration of chloride ion using eq. 12.[2] The total final concentration of KCl was used instead of the total incremental concentration for each particular point in the titration. Using the data given in the paper,[2] but in the proper fashion, the values of the association constants β_1 and β_2 are 96 ± 11 kg./mole and 16 ± 12 kg.^{2}/mole^2, respectively.

It will be noted that the error limits for each of the constants are quite large, especially that for β_2. These are larger than the limits reported earlier for the incorrect constants. It appears now, from an experimental point of view, that the graphical method of Leden, when calculated properly, does lead to rather large errors, as has been suggested earlier.[4]

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(1) J. Braunstein, University of Maine, private communication.

(2) H. T. Tien and G. W. Harrington, *Inorg. Chem.*, **3**, 215 (1964).

(3) J. Braunstein and A. S. Minano, *ibid.*, **3**, 218 (1964).

(4) J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).