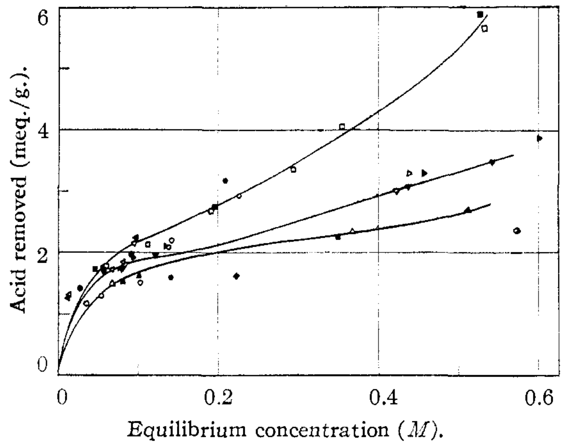

Fig. 2.—Equilibria at two temperatures for Nalcite SAR and the acids: ▷, butyric; □, α-chloropropionic; ○, β-chloropropionic; △, crotonic; ◇, formic; ▽, isobutyric; △, propionic at 30.3°; corresponding symbols filled in represent the same acids at 18.0°. Curves are drawn in to fit the data for α-chloropropionic, isobutyric and propionic.

curves for the second series, obtained with resin processed in a different batch, show lower concentrations in the resin for corresponding solution concentrations, no doubt due to a less complete conversion of resin to hydroxide during the processing. That the acid removal beyond resin capacity is greater for crotonic acid and the chloropropionic acids than for butyric and isobutyric shows that acid removal beyond capacity by this resin is favored by unsaturation and substitution of chlorine for methyl groups. That the measurements at 18.0 and 30.3° for any one acid fit the same curve within the reproducibility of the measurements shows a negligible temperature coefficient for the process. The heat of neutralization of a carboxylic acid by a strong base is not small, although different energies of hydration of the ions in the resin phase than in water may make the heat of neutralization by the resin considerably different than that by aqueous hydroxide ion. It appears that the added process which contributes a large part of the equilibrium has little heat effect.

While adsorption is suggested as this added process, a perhaps more plausible process is the distribution of un-ionized acid between the water within the resin granules and the water outside the resin. This picture is consistent with the approximate linearity of the high concentration parts of the isotherms and the small temperature coefficient of the equilibrium. Adsorption, probably of this same nature, has recently been found[5] to be an important factor in some cation exchange equilibria.

It appears that our original purpose, the correlation of the equilibria of formation of resin carboxylates with anion structure, could have been served better by equilibration of the resin chloride with solutions of salts as has been done for a variety of other anions by Wheaton and Bauman.[2] The lack of sensitivity of our method at low concentrations, the instability of the resin hydroxide as indicated by darkening on standing and the removal of acid without complete neutralization by the resin prevent such a correlation. The last of these three is a new phase of the behavior of resins of this type in contact with acid solutions.

Acknowledgment.—This work was performed under a contract with the Atomic Energy Commission. We are indebted to the College of Arts and Sciences Research Fund for some support, to the National Aluminate Corporation for a generous sample of the resin, to the Tennessee Eastman Corporation for a sample of crotonic acid and to Mr. John Mason and Mr. Merle Likens for preliminary experiments.

DEPARTMENT OF CHEMISTRY
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RECEIVED JULY 17, 1951

Formation of Ether by Association of Alkyl and Alkoxy Free Radicals

BY JOHN H. RALEY AND DAVID O. COLLAMER, JR.

Coexisting alkoxy and alkyl free radicals undergo various reactions including alkyl–alkyl association, hydrogen atom transfer, and decomposition of the alkoxy radicals.[1-3]

A priori it might be expected that, under proper conditions, these two types of radicals would also associate to form an ether. Previous attempts in this Laboratory to isolate an ether from the decomposition products of di-*t*-alkyl peroxides have been unsuccessful. This note, however, reports the identification of methyl ethyl ether as a product of the pyrolysis of methyl *t*-amyl peroxide, a source of methoxy and ethyl radicals. The ether is believed to arise from an association process rather than from attack of either radical on the peroxide, since the latter reaction is known to result in hydrogen atom transfer.[4] It is clear from the ether yield, however, that under the stated conditions reactions of the radicals other than ether formation predominate. It is not surprising, hence, that experiments with the less thermally stable *t*-alkoxy radicals failed to produce detectable amounts of ethers.

Experimental

Methyl *t*-amyl peroxide was prepared by adding dimethyl sulfate to an aqueous solution of the potassium salt of *t*-amyl hydroperoxide. The distilled product (b.p. 32° (60 mm.), n^{20}_{D} 1.3924; C, 61.5; H, 12.3; equivalent weight by reaction with HI, 65.8; theoretical values, respectively, 60.98, 11.94 and 59.09) contained no hydroxyl, carbonyl, ethylenic or aromatic groups detectable by an infrared examination.

The peroxide and nitrogen, in a molar ratio of 2:3, were passed through an unpacked Pyrex tube at 195°. Complete decomposition occurred during the two-minute residence time. The effluent was conducted through a water scrubber and traps held at about 0 and −70°. The remaining vapor, together with that evolved from the receivers upon subsequent warming to room temperature, was collected and analyzed by Orsat and mass spectrometric procedures. The combined liquid from the receivers was then distilled and the various fractions analyzed by standard procedures.

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Methyl ethyl ether was obtained as a fraction distilling at 7–14° (75% at 7–9°). Identification was made by a molecular weight determination and a comparison of the infrared absorption spectrum in the 2–15 μ region with that of an authentic sample. An additional amount was identified in the vaporous product by mass spectrometric comparison with the authentic sample (for example, the ratio of the intensity for ions of $m/q = 31$ to that for ions of $m/q = 60$ was 0.68 for both the reaction product and the known).

The amounts of the various products obtained, in moles per mole of peroxide decomposed, were: $(CH_3)_2CO$ (0.78), CH_3OH (0.29), H_2CO (0.25), C_2H_6 (0.21), CO (0.12), n-C_4H_{10} (0.11), $CH_3COC_2H_5$ (0.093), $C_2H_5C(CH_3)_2OH$ (0.086), *$CH_3OC_2H_5$* (*0.078*), C_2H_4 (0.077), C_3H_8 (0.061), H_2 (0.039), CH_4 (0.036) and C_4H_8 (0.007).

Acknowledgment.—We wish to thank Mr. W. R. Harp, Jr., and Dr. D. P. Stevenson of this Company for supplying the necessary infrared and mass spectral data.

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA
RECEIVED SEPTEMBER 4, 1951

The Ternary System Thallous Sulfate-Sodium Sulfate-Water at 25 and 45°

BY JOHN E. RICCI AND JACK FISCHER

The solubility isotherms at 25 and 45° for the system Tl_2SO_4–Na_2SO_4–H_2O were determined for comparison with the corresponding system Ag_2SO_4–Na_2SO_4–H_2O.[1] In contrast with the continuous solid solution of silver sulfate and anhydrous sodium sulfate, the thallous salt forms no solid solution with the sodium salt at these temperatures.

The materials and the procedure used were those already described in a report on a number of other systems involving thallous sulfate.[2] Complexes prepared from pure Tl_2SO_4 and C.P. Na_2SO_4 were brought to equilibrium and the saturated solution was then analyzed for total solid and for thallium. The mixtures at 25° were seeded with $Na_2SO_4 \cdot 10H_2O$ after the first 24 hours of stirring. In this connection it was noted that the solutions had to be saturated with the sodium sulfate, prior to the seeding with the decahydrate, in order to initiate the precipitation of the new phase, the seed otherwise dissolving without effect. The mixtures were stirred for 7 to 38 days before analysis of the solution, and attainment of equilibrium was proved by constancy of composition on reanalysis after further stirring.

The measurements, in terms of weight percentage, are listed in Table I for the two temperatures studied, and those for 45° are plotted in the usual fashion in Fig. 1. According to the tie-lines the only solid phases formed are the pure salts, Tl_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ at 25°, Tl_2SO_4 and Na_2SO_4 at 45°. The average absolute error from the compositions of the pure solids, calculated by algebraic extrapolation of the 14 tie-lines involved, is only 0.23% (with 0.77 maximum) on the phase diagram.

The solubility of $Na_2SO_4 \cdot 10H_2O$ at 25° is seen to be hardly affected by the Tl_2SO_4, although that of the anhydrous Na_2SO_4 at 45° does suffer the expected decrease. The solubility of Tl_2SO_4 at both temperatures, on the other hand, is distinctly increased by Na_2SO_4, suggesting the formation of some complex involving thallous sulfate and sulfate ion. Potassium oxalate similarly increases the solubility of thallous oxalate.[3]

TABLE I

SYSTEM $Tl_2SO_4(A)$–$Na_2SO_4(B)$–$H_2O(W)$

Complex % A	Complex % B	Solution % A	Solution % B	Density	Solid phase
		Temperature: 25°			
...	0.00	5.222	0.00	1.046	A
19.49	4.89	6.24	5.69	1.112	A
14.97	9.98	7.32	10.87	1.178	A
12.45	15.21	8.06	15.95	1.245	A
14.99	16.98	8.27	18.34	1.275	A
13.99	21.97	8.48	21.23	1.313	A + B·10W
7.98	27.99	8.42	21.34	1.315	A + B·10W
5.47	25.37	6.59	21.50	1.290	B·10W
3.51	25.98	4.36	21.56	1.256	B·10W
1.41	26.11	1.77	21.58	1.219	B·10W
0.00	...	0.00	21.66	1.210	B·10W
		Temperature: 45°			
...	0.00	7.73	0.00	1.064	A
20.02	7.00	9.62	8.00	1.166	A
20.22	13.07	10.86	14.65	1.254	A
17.94	16.96	11.32	18.39	1.308	A
20.03	19.96	11.41	22.11	1.356	A
18.02	27.00	11.05	28.80	1.434	A + B
11.68	32.43	11.04	28.78	1.435	A + B
10.02	35.07	10.95	28.75	1.434	B
7.50	37.50	8.46	29.57	1.399	B
4.96	39.89	5.74	30.42	1.362	B
0.00	...	0.00	32.05	1.308	B

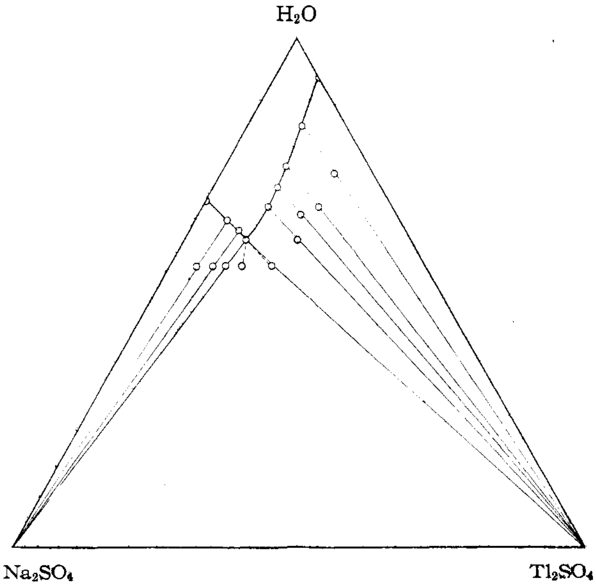

Fig. 1.—System Tl_2SO_4–Na_2SO_4–H_2O at 45°.

Silver and thallous sulfates form solid solutions, besides a 1:1 compound, in their binary system at the melting curve.[4] At room temperatures, however, the argentous salts form solid solutions with various corresponding sodium salts (sulfate,[1] bro-

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