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Characterization and Some Reactions of Peroxy-*trans*-crotonic Acid[1a]

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Peroxy-*trans*-crotonic acid was prepared from dicrotonyl peroxide by alkaline cleavage and isolated for the first time in a crystalline state, mp 41—42°C. It was characterized by NMR and IR spectra, and its stability briefly tested. Reaction with dimethyl sulfide gave a quantitative yield of crotonic acid. Its pK_a in water at 25°C was 8.2. Second order rate constants of reaction with crotonaldehyde in benzene (Table 4) were measured: E_a, 13.3 kcal/mol; log A(l/mol sec), 5.3; $\Delta S^{\neq}$, -36 eu/mol. Detection of a possible intermediate, a peracid-aldehyde complex X, was attempted by means of NMR but evidence for it was not obtained.

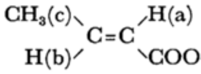
Peroxycrotonic acid, first prepared by Fichter and Rosenzweig[2] in an impure liquid form, has remained unidentified, although it has been reasonably assumed to be identical with, and appeared in chemical literature as, the peroxidic intermediate of vapor phase[3] and liquid phase[4] autoxidation of crotonaldehyde. Recently some infrared absorption bands were ascribed to the peroxycrotonic acid that was believed to be formed transiently in the course of autoxidation of crotonaldehyde.[5]

We wish to describe the preparation, characterization, and some reactions of peroxy-*trans*-crotonic acid.

Results and Discussion

Peroxycrotonic acid was prepared from dicrotonyl peroxide by cleavage with sodium methoxide. It is necessary to handle the alkaline solution of the peracid quickly and in the cold, as in the preparation of peroxybenzoic acid,[6,7] in order to get satisfactory results. Peroxycrotonic acid forms colorless needle crystals which melt at 41—42°C with slow decomposition and flash vividly in free flames. The crystals are stable against fairly strong mechanical shock. In crystalline state the peracid could be stored for longer than one year at −70°C without appreciable deterioration, while at 0—5°C the loss of peroxidic oxygen amounted to 0.5, 4.9, and 14% after periods of 38, 55, and 82 days, respectively. In benzene solution (0.45 M) at 30°C the decrease of the iodometric titre was about 1.7% per day in the first week, indicating that its stability is greater[8] than that of peroxybenzoic acid[7] under the same conditions.

Table 1. NMR Parameters of crotonic acid derivatives



$$\begin{matrix} CH_3(c) \diagdown & & \diagup H(a) \\ & C{=}C & \\ H(b) \diagup & & \diagdown COO- \end{matrix}$$

	Peroxycrotonic acid[a)]	Dicrotonyl peroxide[a)]	Crotonic acid[b)]
τ_a	4.15	4.13	4.17
τ_b	2.88	2.89	2.90
τ_c	8.03	8.03	8.10
τ_d[c)]	−0.67	—	−2.18
J_{ab}	16 cps	15.5 cps	15.5 cps
J_{bc}	7	7	7
J_{ac}	1.5	1.6	1.6

a) 10 wt % solution in carbon tetrachloride containing tetramethylsilane as internal standard.

b) In $CDCl_3$, quoted from Varian NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 61.

c) The chemical shift of acidic protons.

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[1] a) Peroxyacid. I. Presented in part at the 21st Annual Meeting of the Chemical Society of Japan, Suita, Osaka, April 1968; Abstract, p. 1630. b) To whom inquiries should be addressed.

[2] F. Fichter and J. Rosenzweig, *Helv. Chim. Acta*, **18**, 238 (1935).

[3] J. Cartlidge and C. F. Tipper, *Anal. Chim. Acta*, **22**, 106 (1960).

[4] Kirk-Othmer, "Encyclopedia of Chemical Technology," Vol. 6, 2nd ed., Interscience Publishers, New York, N. Y. (1965), p. 466.

[5] X. Deglise and J. Lemaire, *J. Chim. Phys.*, **64**, 1768 (1967).

[6] G. Braun, "Organic Syntheses," Coll. Vol. I, 2nd Ed., p. 431 (1948).

[7] I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).

[8] The comparison is only tentative since peracid stability is easily influenced by contamination of metallic impurities.

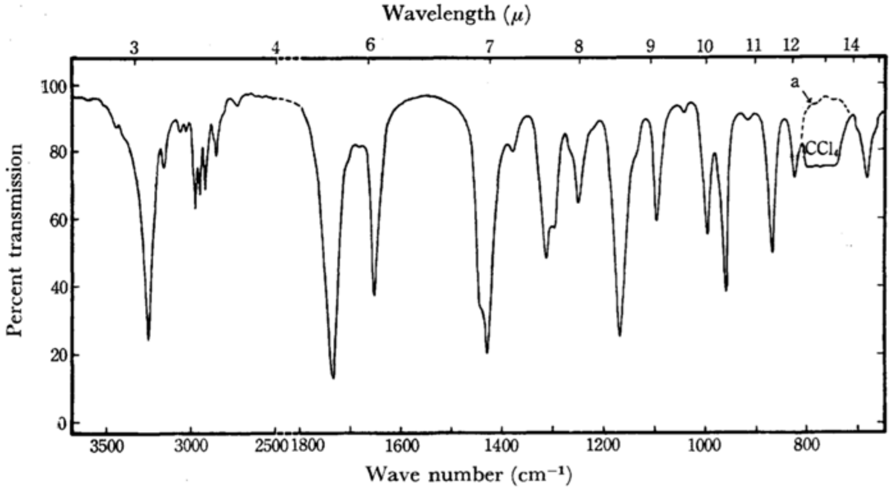

Fig. 1. Infrared absorption spectrum of peroxy-*trans*-crotonic acid in CCl_4: 650—2000 cm^{-1}, 1.0 mol/*l*, 0.025 mm optical length: 2000—4000 cm^{-1}, 0.25 mol/*l*, 0.1 mm optical length. Solvent absorptions are compensated, except in the region 720—810 cm^{-1} where the peracid has no absorption bands in CS_2 solution (curve a), by adjusting the optical length of CCl_4 reference.

Peroxycrotonic acid can be identified by the following observations, 1) the wt% of its peroxidic oxygen agrees with the calculated value, 2) it is quantitatively converted to crotonic acid by reduction with dimethyl sulfide, and 3) its NMR and IR spectra are consistent with the assigned structure.

The NMR parameters are listed, together with those for dicrotonyl peroxide and crotonic acid as authentic references, in Table 1.

The infrared absorption spectrum and the tentative assignment[9] of the principal bands are shown in Fig. 1 and Table 2, respectively. Many of the absorption bands agree with those reported by Deglise and Lemaire[5] for the peroxycrotonic acid intermediate of the autoxidation of crotonaldehyde (Table 2), supporting identity of the substance.

The pK_a of peroxycrotonic acid in water at 25°C (pH of half neutralization) was found to be 8.15. When correction for ionic strength was made, it was calculated to be 8.21. However, it should be noted that pK_a determination of peroxyacids by the acidimetric titration method cannot be accurate since the compounds are unstable.[10] As an example of the present determinations, 15% of the initial peroxidic activity had been lost when pH determination at half neutralization point was finished (in about 15 min at 25°C). Although the pK_a value should be taken as approximate, it is comparable with those of some other peracids as shown in Table 3. The difference in acid strength of a peroxyacid and the parent carboxylic acid is around 3.4 in pK_a units on the average.[11]

The rate of reaction of peroxycrotonic acid with crotonaldehyde in benzene solution forming two moles[*1] of crotonic acid was measured by iodometric determination of the remaining peracid. The rate followed the second order kinetics, first order in both reactants, with no induction period within experimental error (Fig. 2). The decrease of the rate caused by the addition of 1,3,5-trinitrobenzene, a stronger inhibitor of radical chain reaction,[12] was real, but to an extent that would permit us to neglect the induced decomposition of the peracid in evaluation of the rate data (Table 4). The least-squares treatment of the Arrhenius equation afforded the following parameters of activation: E_a, 13.3±0.5 kcal/mol; log A (*l*/mol sec), 5.3±0.5

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[9] For the basis of the assignment see Ref. 5, as well as W. V. F. Brooks and C. M. Haas, *J. Phys. Chem.*, **71**, 650 (1967); D. Swern and L. S. Silbert, *Anal. Chem.*, **35,** 880 (1963); and R. Kavcic, B. Plesnicar and D. Hadzi, *Spectrochim. Acta*, **23A**, 2483 (1967).

[10] a) J. F. Goodman, P. Robson and E. R. Wilson, *Trans. Faraday Soc.*, **58,** 1846 (1962). b) E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H.Y. Ryun and J. O. Edward, *J. Am. Chem. Soc.*, **85,** 2263 (1963). c) K. Akiba and O. Simamura, *Chem. Ind. (London)*, **1964**, 705.

[11] This relation was used in estimation of pK_a of peroxytrifluoroacetic acid; W. D. Emmons and P. S. Pagona, *J. Am. Chem. Soc.*, **77**, 89 (1955).

[*1] Over 90% yield of crotonic acid based on reacted crotonaldehyde is obtained by autoxidation of crotonaldehyde at 40% conversion (unpublished work); see also H. Inoue, H. Ito, and K. Takahashi, *Kogyo Kagaku Zasshi*, *(J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **71**, 1862 (1968). This shows that the intermediate peroxycrotonic acid reacts with crotonaldehyde to give two moles of crotonic acid in an almost quantitative yield, with practical exclusion of formation of 1-propenyl formate.

[12] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5428 (1950).

Table 2. Assignment of infrared absorption bands of peroxy-*trans*-crotonic acid

Observed (cm^{-1})	Assignment	by Ref. 5
3266	ν_{O-H}	3262
1736	$\nu_{C=O}$	1730
1656	$\nu_{C=C}$	1656
1443	δ_{CH_3} asym.	—
1434	δ_{O-H} in plane	1431
1382	δ_{CH_3} sym.	—
1311	δ_{C-H} (sp^2) in plane	1308
1297		—
1252	ν_{C-O}	1260
1170		—
1098		1103
994	δ_{C-H} (sp^2) out of plane	990
965	δ_{O-H} out of plane	—
871	ν_{O-O}	873

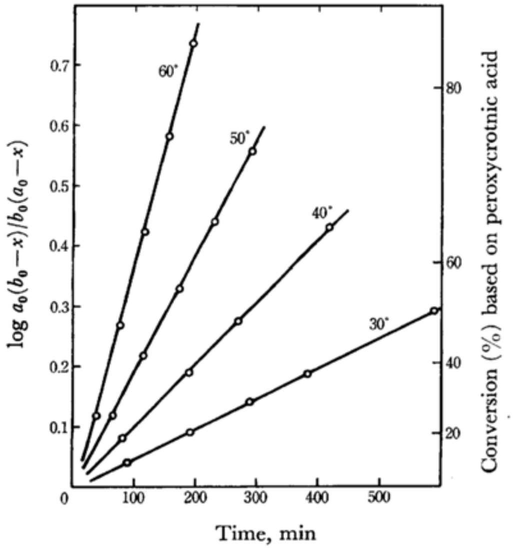

Fig. 2. Representative kinetic runs.

Table 3. pK_a values of some peroxyacids and the parent carboxylic acids in water[a]

	Temp. °C	pK_a Peroxyacid	pK_a Acid	ΔpK_a
Formic	20	7.1	3.75	3.3
Acetic	20	8.2	4.76	3.4
Chloroacetic	25	7.2[b]	2.87	4.3
Propionic	23	8.1	4.88	3.2
n-Butyric	21.5	8.2	4.81	3.4
Crotonic	25	8.2[c]	4.66	3.5
Benzoic	25	7.78[d]	4.20	3.6

a) *cf.* "Landolt-Börnstein, Zahlenwerte und Funktionen," 6th ed, Springer-Verlag, Berlin (1960), Vol. 2, Part 7, p. 847 for the unannotated figures.
b) E. Koubek and J. O. Edward, *J. Org. Chem.*, **28**, 2157 (1963).
c) The present work.
d) J. F. Goodman, P. Robson and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).

Table 4. Rate constants of reaction of peroxycrotonic acid with crotonaldehyde

Temp. °C	a_0[a] mol/l	b_0[b] mol/l	TNB[c] mol/l	k (l/mol sec) $\times 10^4$
30	0.0532	0.504	0	0.432
	0.0489	0.254	0	0.415
	0.0563	0.506	0	0.436
	0.0489	0.509	0.0175	0.407
40	0.0457	0.505	0	0.872
	0.0457	0.505	0.0176	0.832
50	0.0505	0.498	0	1.68
	0.0505	0.498	0.0176	1.63
60	0.0568	0.507	0	3.28
	0.0492	0.507	0.0173	3.08

a) Initial concentration of peroxycrotonic acid.
b) Initial concentration of crotonaldehyde.
c) 1,3,5-Trinitrobenzene added.

(in the absence of trinitrobenzene): and E_a, 13.5±0.1 kcal/mol; log A (l/mol sec), 5.4±0.1 (in the presence of trinitrobenzene).[13]

From these results we could regard the reaction as a simple bimolecular reaction, where a highly ordered alignment of the reactants in the transition state is implied by the small pre-exponential factor A ($\Delta S^{\ddagger}=-36$ eu/mol) comparable to that of the Diels-Alder reactions.

Further considerations as to the course of the reaction seem to be required. It is known that peracetic acid and acetaldehyde react to form an isolable complex, "AMP" (X: R=CH_3),[14] which eventually transforms to two moles of acetic acid. Similar intermediates have been shown spectrometrically in the peroxyheptanoic acid - heptaldehyde[15] and peroxycrotonic acid - heptaldehyde[5] cases. In the cases of peroxybenzoic acid - benzaldehyde and peroxycrotonic acid - crotonaldehyde pairs, however, direct search by infrared spectrometry for the intermediate, X, turned out to be negative,[5,15,16] although X (R=phenyl) was assumed as an intermediate from kinetic studies.[17] Whether

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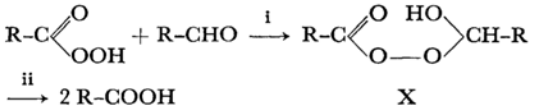
13) The attached ranges are limits of 95% confidence of the regression analysis.

14) B. Phillips, F. C. Frostic, Jr., and P. S. Starcher, *J. Am. Chem. Soc.*, **79**, 5982 (1957).

15) J. C. André, J. F. Large, X. Deglise, J. Lemaire and M. Niclause, *Rev. Inst. Fr. Petrole Ann. Combust. Liquides*, **23**, 219 (1968).

16) C. R. Dick and R. F. Hanna, *J. Org. Chem.*, **29**, 1218 (1964).

17) Y. Ogata, I. Tabushi and H. Akimoto, *ibid.*, **26**, 4803 (1961).



X can accumulate to a detectable concentration or not depends evidently on the ratio of rates of steps i and ii of the particular system under investigation. In an extreme case the structure X can be a representation of the transition state of a single step reaction.

An attempt to detect X (R=CH_3CH=CH–) by NMR was made. As an example, a solution of peroxycrotonic acid (2M) and crotonaldehyde (2M) in methyl acetate was stored at 0°C for 76 hr to accomplish a half conversion of the reactants and the NMR spectrum was taken. No extra absorption, other than those from the reactants and crotonic acid, were observed. A critical examination of the spectrum in order to find an upper limit of the steady state concentration of X did not give a definite conclusion, but it seems that X very probably does not exist in a considerable concentration. This result is in accord with the conclusion by Deglise and Lemaire[5)] based on infrared spectroscopic studies.

The contrast between the behavior of saturated aldehydes and the α,β-unsaturated and aromatic aldehydes with regard to the intermediacy of X is ascribed partly to the reduced rate of step i in the latter, because of the loss of conjugative stabilization of the carbonyl group in transforming into hemi-acetal structure X. The effect of unsaturation to the rate of step ii cannot be predicted. From failure to detect X it is inferred that step i is slower than step ii, if X is an unstable intermediate in contrast to the transition state. However, the possibility that a rapid equilibrium between the reactants and X, together with step ii, may give an undetectable steady state concentration of X, cannot be ruled out.[18)]

Experimental[19)]

Dicrotonyl peroxide was prepared by the method of Tuerck[20)] and was purified by recrystallization from petroleum ether; mp 41.3—42.3°C, lit mp 40—41°C,[20)] mp 41°C.[2)] The peroxidic oxygen as determined by the iodometric titration for dibenzoyl peroxide[6)] was 97.9% of the theoretical.

Preparation of Peroxycrotonic Acid. A solution of 17.0 g (0.10 mol) of dicrotonyl peroxide in 70 m*l* of chloroform was placed in a round bottomed flask equipped with a loosely fitted thermometer, and was cooled in a dry ice-acetone bath. To this solution (at *ca.* −65°C) was added an ice cold methanolic sodium methoxide solution, prepared from 2.4 g (0.105 g atom) of sodium and 20 m*l* of absolute methanol, in less than 1 min with swirling. The flask was vigorously shaken in the bath for several seconds and was transferred into an ice-salt bath (−5°C) in which it was vigorously shaken for 4 min.[21)] The solution was immediately poured onto 250 g of water containing chopped ice in a separatory funnel, the sodium peroxycrotonate extracted quickly into the aqueous layer, and the chloroform discarded. After washing with two successive 50 m*l* portions of cold chloroform, the aqueous solution was admixed with 50 m*l* of chloroform and 120 g of 5% aqueous sulfuric acid, and the peroxycrotonic acid was extracted with three further 50 m*l* portions of cold chloroform. The combined chloroform extracts were washed twice with water, dried with anhydrous sodium sulfate, and the chloroform was evaporated in a vacuum by a water aspirator to obtain 10 g of white solid of crude peroxyacid as residue. The solid was recrystallized from 100 m*l* of petroleum ether, bp 40—60°C, to obtain fine needles. After storing overnight in a refrigerator, the crystals, 4.5 g, were collected by suction filtration under dry atmosphere: mp 41—42°C. Further crops, 1.4 g, were obtained from the filtrate: total yield, 57.8% of the theory. When the petroleum ether suspension of the peroxyacid is stored in a refrigerator for a week, massive crystals which are easier to handle are obtained.

In a run of smaller scale (0.02 mol) the alkaline cleavage reaction was carried out in an ice bath with similar yield of the product.

The purity of the specimen was determined to be nearly 100% by the iodometric titration or the wt % of the peroxidic oxygen was found to be 15.57%: Calcd for $C_4H_6O_3$, 15.67%.

Reaction with Dimethyl Sulfide. Dimethyl sulfide, 1.0 m*l*, was added dropwise to 1 m*l* of ethyl acetate solution of 0.0450 g of peroxycrotonic acid in a dry ice-acetone bath. After standing in a refrigerator for 1 hr the solution was treated with a slight excess of ethereal diazomethane at −70°C, and was kept overnight at this temperature. The methyl crotonate formed was determined to be 96—99% of theory by quantitative glpc analysis using ethylbenzene as the internal standard. Esterification with diazomethane at 0°C gave erratic results presumably because of the pyrazoline formation.[22)]

Kinetic Measurements.[23)] A 200 m*l* two-mouthed

[18)] When this mechanism is adopted the net forward rate of step i should mean the rate of step i of the foregoing description.

[19)] Melting points are corrected. NMR spectra were taken using a Varian A-60A spectrometer. IR spectra were recorded on a Nihon Bunko Model DS-402G double-beam grating spectrophotometer. A Hitachi-Horiba glass electrode pH meter type M-5, calibrated with pH standard solutions, was used for pH determinations.

[20)] K. H. W. Tuerck, U. S. Pat. 2379390 (1945); *Chem. Abstr.*, **39**, 4620 (1945).

[21)] In a few runs in which this procedure was allowed to continue for about 10 min, very poor results were obtained.

[22)] a) A. Ledwith and D. Parry, *J. Chem. Soc., C*, **1966**, 1408. b) T. V. Van Auken and K. L. Rinehard, Jr., *J. Am. Chem. Soc.*, **84**, 3736 (1962).

[23)] Commercial crotonaldehyde was dried with anhydrous calcium sulfate and rectified under nitrogen stream; bp 42°C/83 mmHg. Benzene was purified by treatment with concentrated sulfuric acid, dried with calcium chloride, and was distilled from sodium wire.

flask, fitted with a gas-inlet and a stopper, was flushed with dry nitrogen and 50 m*l* of a benzene solution of crotonaldehyde was added and thermostated. While a slow stream of nitrogen, saturated with benzene vapor, was bubbled through the solution, a 50 m*l* benzene solution of peroxycrotonic acid was added to start the reaction, and the system was stoppered under a slight pressure of nitrogen. After appropriate time intervals an aliquot of 10 m*l* was taken out into a flask containing 2 g of potassium iodide, 45 m*l* of water, 5 m*l* of acetic acid, 10 m*l* of chloroform, and a few pieces of dry ice. The liberated iodine was immediately titrated with a standard sodium thiosulfate solution: the end-point was sharp.