salt is seen to differ slightly from the effect of sodium acetate.

The thermodynamic solubility exponent, pS, can be obtained by extrapolation to zero ionic strength of the graph of pS' against $\sqrt{\mu}$. However, this extrapolation gives the greatest weight to the least accurate determinations, *i. e.*, those at low ionic strength. A better method of finding pS involves the use of the equation

$$pS = pS' - 2 \log f_{\pm}$$

where $f_{\pm}$ denotes the mean activity coefficient of the ions of the barium chromate. Values of $f_{\pm}$ may be calculated by the use of the equation of Gronwall, LaMer and Sandved.[4] The last column in Table I shows the pS values thus calculated on the assumption that a = 4.3 Å. This radius was chosen because it yields the most consistent pS values for sodium acetate as the solvent salt. It is in good agreement with the mean value (4.5 Å.) of the effective radii of the barium and chromate ions as given by Kielland.[5]

Barium chromate differs markedly from strontium chromate in the time required to establish solubility equilibrium. Whereas two hours suffice for barium chromate, it is reported[6] that over a year is required for strontium chromate.

In the separation of barium from strontium by the standard method[7] of precipitating barium chromate, it was found that the pH is about 5.7. From the data presented in this paper along with the values[8] for the equilibrium constants of the reactions

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^=$$
$$2HCrO_4^- \rightleftharpoons Cr_2O_7^= + H_2O$$

it can be calculated that a quantitative precipitation of barium should occur at a much lower pH, about 4.6. The application of this lower pH should give a precipitate with much less coprecipitated strontium, thus improving the separation. This point is now under investigation.

Summary

The solubility product of barium chromate at ionic strengths up to 0.25 has been determined. The results are in good agreement with the extended Debye–Hückel equation.

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[4] Gronwall, LaMer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[5] Kielland, THIS JOURNAL, **59**, 1675 (1937).

[6] T. W. Davis, *Ind. Eng. Chem., Anal. Ed.*, **14**, 709 (1942).

[7] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 492.

[8] Neuss and Rieman, THIS JOURNAL, **56**, 2238 (1934).

NEW BRUNSWICK, N. J. RECEIVED OCTOBER 19, 1942

[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Absorption of Light by 1,5-Dien-3-ynes in the Region 2300–2900 Å.[1]

BY HARRY BASTRON, RUSSELL E. DAVIS AND LEWIS W. BUTZ

The characteristic ultraviolet absorption curves of 1,5-dien-3-ynes have not yet been reported. Determination of the curves of certain polycyclic adducts of these hydrocarbons has yielded valuable information concerning the structure of the adducts.[2] The latter are obtained mixed with by-products which are quantitatively important and the composition of which, if known, might suggest something about the dienyne addition reactions. Conceivably, adducts might be formed which contain the 1,5-dien-3-yne system as part of their structure. For this reason the absorption of a series of dienynes has been determined. The group examined consisted of one open-chain, two monocyclic, and four bicyclic dienynes.

Six of the dienynes were prepared in our own Laboratory by the dehydration of the corresponding ethynylenediols with hot aqueous mineral acid. The seventh, a methoxy dienyne, was given to us by Dr. C. S. Marvel whose generosity it is a pleasure to acknowledge.

The dienynes, prepared according to the published procedures (see table), are yellow liquids. The yellow cyclohexenylcyclopentenylacetylene was refluxed with potassium hydroxide in ethanol, and in this way a colorless preparation was obtained.[3] The curve of this colorless sample is very similar to the curve of a yellow sample of the closely related methoxy derivative (Curves 5 and

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[1] This work was supported in part by an allotment from the Special Research Fund (Bankhead-Jones Act of June 29, 1935). Not subject to copyright.

[2] Butz and Joshel, THIS JOURNAL, **64**, 1311 (1942), and earlier papers.

[3] By Dr. L. M. Joshel.

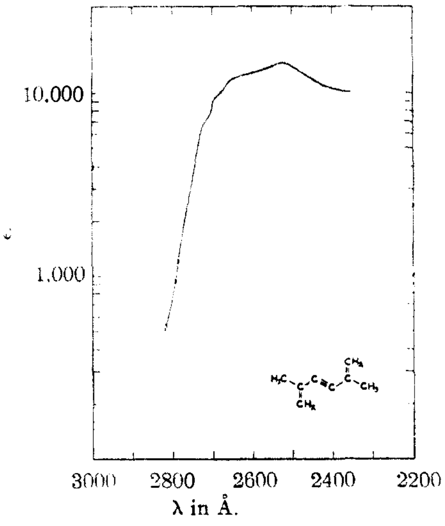

Fig. 1.

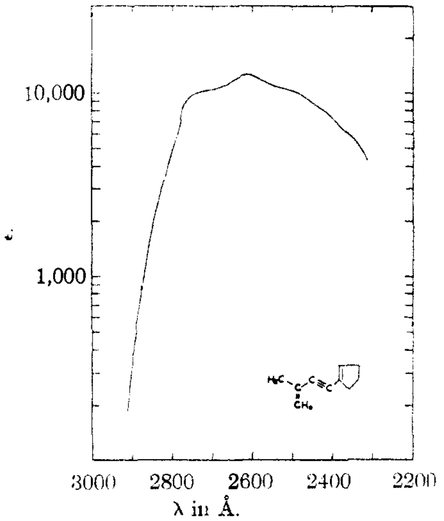

Fig. 2.

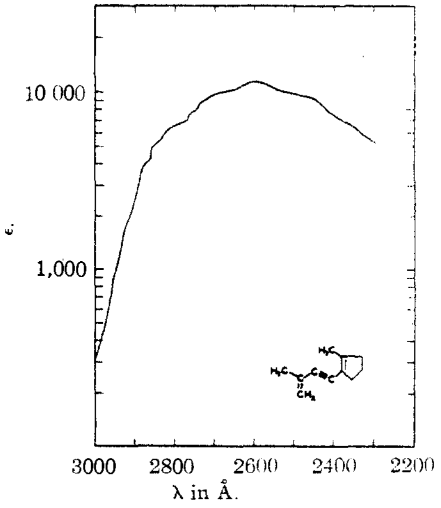

Fig. 3.

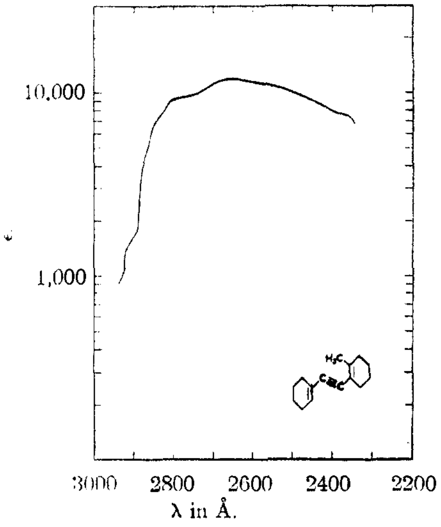

Fig. 4.

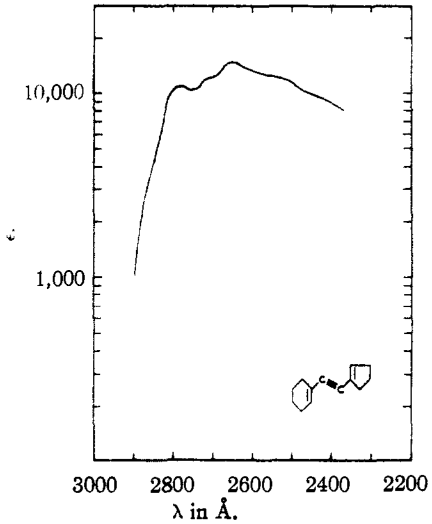

Fig. 5.

6). The 1-cyclopentenylisopropenylacetylene and isopropenyl-(2-methyl-1-cyclopentenyl)-acetylene are new dienynes which were prepared by Dr. W. Nudenberg.[4] The possibility that the two dienynes with methylated rings contain two isomers each (see footnotes to table) cannot be excluded on available evidence.[5]

Absorption data for two 1,3,5-trienes, related to the dienynes, have been taken from the literature and included in the table. The principal maximum for the trienes is at longer wave lengths and maximal absorption is considerably more intense than that for the dienynes. A comparison of the dienynes among themselves shows that,

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[4] Unpublished.

[5] Joshel, Butz and Feldman, THIS JOURNAL, **63**, 3348 (1941), and ref. 4.

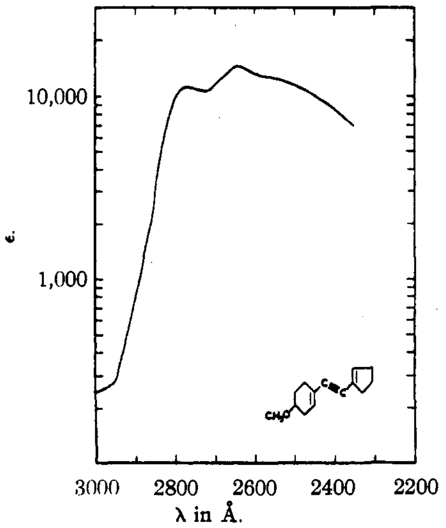

Fig. 6.

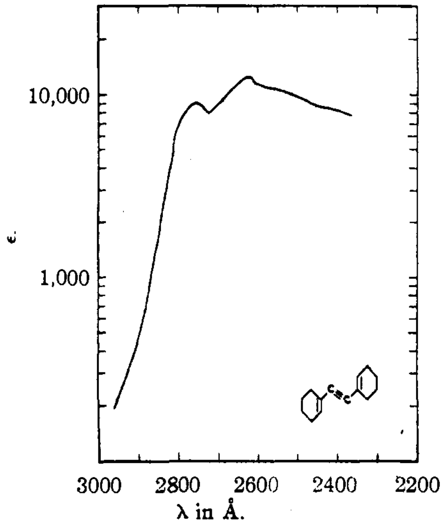

Fig. 7.

TABLE I

Acetylene	Curve	$\lambda_{max.}$ (Å.)	ε	Boiling range °C.	Mm.	n_D	Reference
Diisopropenyl	1	2525	14500	82–85	101	1.4857 (22°)	*a*
Cyclopentenylisopropenyl	2	2615	13000	81	13	1.5332 (21°)	*b*
Isopropenyl-2-methylcyclopentenyl[c]	3	2600	11500	90	14	1.5103 (27°)	*b*
Cyclohexenylcyclopentenyl	5	2650[d]	15000	110–113	1	1.5616 (21°)	*e*
4-Methoxycyclohexenylcyclopentenyl	6	2645[f]	14750	136	1.5		*g*
Dicyclohexenyl	7	2625[h]	12500	130	2	1.5501 (23°)	*e*
Cyclohexenyl-2-methylcyclohexenyl[i]	4	2650	12000	118–121	0.5	1.5469 (21°)	*j*

Ethylene	$\lambda_{max.}$ (Å.)	ε	Reference
α,β-Diisopropenyl	2611[k]	45600	*l*
α,β-Dicyclohexenyl	2690	22900	*m*

[a] Mitchell and Marvel, THIS JOURNAL, **55**, 4277 (1933). [b] Reference 4. [c] May contain some 5-methyl isomer. [d] Minimum, 2750 Å.; ε, 10500. Second maximum, 2780 Å.; ε, 11500. [e] Pinkney, Nesty, Wiley and Marvel, THIS JOURNAL, **58**, 972 (1936). [f] Minimum, 2720 Å.; ε, 11000. Second maximum, 2770 Å.; ε, 11500. [g] Marvel and Walton, *J. Org. Chem.*, **7**, 88 (1942). [h] Minimum, 2725 Å.; ε, 8000. Second maximum, 2755 Å.; ε, 9000. [i] May contain some 6-methyl isomer. [j] Marvel, Mozingo and White, THIS JOURNAL, **62**, 1880 (1940). [k] Other maxima at 2512 Å. (ε, 33660) and at 2717 Å. (ε, 36800). [l] Calculated from the data reported by Kharasch, Nudenberg and Sternfeld, THIS JOURNAL, **62**, 2036 (1940). [m] Burkhardt and Hindley, *J. Chem. Soc.*, 987 (1938); from the compilation by Dimroth, *Angew. Chem.*, **52**, 555 (1939).

going from the open-chain dienyne through the monocyclic to the bicyclic dienynes, the principal maxima are found at longer and longer wave lengths.

A Bausch and Lomb large Littrow quartz spectrograph equipped with a sector photometer was used in determining the ultraviolet absorption curves of these compounds. A condensed spark between high-speed steel electrodes served as light source. The freshly distilled dienynes were dissolved in ethanol.

Summary

Ultraviolet absorption curves for seven 1,5-dien-3-ynes are recorded and a regularity in the position of the chief maximum relative to the number of rings contained in the dienyne system is noted.

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