NOTES.

The 2 : 4-*Dinitrophenylhydrazone of* n-*Valeraldehyde*. By R. S. Airs, D. A. Firth, and P. J. Garner.

Three different values have been recorded for the m. p. of the 2 : 4-dinitrophenylhydrazone of *n*-valeraldehyde : 98° by Allen (*J. Amer. Chem. Soc.*, 1930, **52**, 2955), 106·5—107° by Backer and Haack (*Rec. Trav. chim.*, 1938, **57**, 225), and 88° by Wienhaus and Mucke (*Ber.*, 1942, **75**, 1830). Standard tables of data quote 98°. In the course of work in this laboratory the 2 : 4-dinitrophenylhydrazone of synthetic *n*-valeraldehyde has been prepared.

n-Amyl alcohol was synthesised from *n*-butyl bromide and trioxymethylene by the method given by Freundler and Damond (*Bull. Soc. chim.*, 1906, **35**, 110) for *sec.*-butylcarbinol ; it had b. p. 137·5—137·7°/767 mm. Heilbron ("Dictionary of Organic Compounds," Eyre and Spottiswoode, 1943, p. 141) gives b. p. 137°/740 mm. The procedure used by Badin and Pacsu (*J. Amer. Chem. Soc.*, 1945, **67**, 1352) for the production of *iso*valeraldehyde was applied to the above alcohol and yielded *n*-valeraldehyde, b. p. 102·5—103·5°/767 mm. Bruylants and Ernould (*Bull. Acad. roy. Belg.*, 1931, **17**, 1174) give b. p. 102·5—103·0°/760 mm.

The 2 : 4-dinitrophenylhydrazone was prepared by the method of Shriner and Fuson ("The Systematic Identification of Organic Compounds," Wiley and Sons, 1940, p. 143) ; it separated from methanol in needles, m. p. 107·6° (corr.) (Found : C, 49·9 ; H, 5·2. Calc. for $C_{11}H_{14}O_4N_4$: C, 49·7 ; H, 5·3%).

The authors wish to thank the N.V. de Bataafsche Petroleum Maatschappij for permission to publish.—B.P.M. Research Laboratories, Thornton-le-Moors, Cheshire. [*Received, March 22nd*, 1946.]

The Reaction between Gaseous cyclo*Pentadiene and Benzoquinone*. By Albert Wassermann.

The kinetics of the gaseous diene synthesis *cyclo*pentadiene (a) +benzoquinone (b) ⟶ *cyclo*pentadiene–benzoquinone (c) has been investigated in vessels of "Pyrex" glass between 125° and 155° and at initial pressures between 15 and 25 mm. Under these conditions the reaction is heterogeneous, which is believed to be due to the fact that (a) and (b) are much less polar than the associated species (c). The dipole moment of (a) has not been determined but it cannot be much more than about 0·3D., since the molecule contains only carbon–carbon and carbon–hydrogen bonds (cf. Smyth, *J. Physical Chem.*, 1937, **41**, 209). The molecule (b) appears to be almost flat (Robertson, *Proc. Roy. Soc.*, 1935, **150**, 106), so the various bond moments should compensate each other and the total dipole moment should be near zero, a conclusion which is not in contradiction with measurements of Hassel and Naeshagen (*Z. physikal. Chem.*, 1929, *B*, **6**, 445), Le Fèvre and Le Fèvre (*J.*, 1935, 1697), Hammick, Hampson, and Jenkins (*J.*, 1938, 1263), and Coop and Sutton (*ibid.*, p. 1269). The dipole moment of (c), on the other hand, is as high as 1·39D. (Le Fèvre and Le Fèvre, *loc. cit.*) owing to the requirements of ring strain keeping the two carbonyl groups rigidly in *cis*-mutual orientation (cf. Fig. 1, *J.*, 1935, 1512). A study of the kinetics of the decomposition of (c) into (a) and (b), carried out by Khambata and Wassermann (*J.*, 1939, 375), led to results which indicate that (c) and the activated complex (ab)* are similar species (cf. Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 143). It is reasonable, therefore, to postulate that in passing from (a) and (b) to (ab)* an increase of polarity takes place. According to this hypothesis the formation of (c) can be compared with the association $NEt_3 + EtI = NEt_4I$ (d), which is also heterogeneous in glass vessels (Moelwyn-Hughes and Hinshelwood, *J.*, 1932, 230) and is supposed to involve relatively strongly polar intermediate configurations (see, *e.g.*, Bell, *J.*, 1943, 632). It follows therefore that in the formation of (c) and (d) the activated complex is characterised by a stronger electrostatic field than the two reactants separately and thus the formation of associated species should be facilitated near a glass surface which can be regarded as a two-dimensional polar liquid. This in turn would give rise to a relatively fast wall reaction which masks the homogeneous association in the gas phase which may be taking place.

It is not within the scope of this paper to compare the mechanism of the formation of (c) and (d) with that of gaseous associations, or of reactions of the type $A + B = C + D$ involving rate-determining steps of unknown stoicheiometric equation. Reference is made, however, to the previously investigated gaseous bimolecular diene syntheses (for a list, see *J.*, 1939, 366) which are all homogeneous. These processes either involve participants which are hydrocarbons, or else one of the reactants is a hydrocarbon and the other an aldehyde, and there is no effect which could be made responsible for a marked difference of polarity between the initial state and the activated complex. It is understandable, therefore, that the polar wall of the reaction vessel does not substantially enhance the formation of the activated complex, and it is believed that for this reason the heterogeneous association does not become predominant.

Experimental.—The rate measurements were carried out by using the apparatus described by Benford and Wassermann (*J.*, 1939, 366). The two 6-l. "Pyrex" flasks were first filled with vapour of carefully purified (b), and then with redistilled gaseous (a), the initial pressure of which was determined by extrapolating the total pressure to the time of mixing and subtracting from this the pressure of (b); the time of mixing was taken to be that when one half of (a) had been distilled into the reaction vessels. It was ascertained that neither the tap grease nor the mercury had a detectable influence on the kinetics. After each experiment the reaction mixture was distilled out and the substances thus obtained were jointly purified by fractional recrystallisation from hexane. *cyclo*Pentadiene–benzoquinone could be isolated and was identified by mixed m. p. In attempting to characterise the rate of addition of gaseous (a) to (b) by second-order velocity coefficients, *v*, it was found that at 125° and 135° the values of *v* increased with time, but at 145°, 153°, and 155° a decrease took place. Typical experiments in "empty" vessels are shown in Table I. The initial pressure of (b) was 5·9 mm. at 125° and 10·7 mm. at 153°.

TABLE I.

125°	Time (mins.)	0	8	13	18	28	43
	Pressure (mm.)	14·6	12·9	12·0	11·0	9·6	8·5
	v (l. g.-mol.$^{-1}$. min.$^{-1}$)	—	130	144	184	264	400
153°	Time (mins.)	0	10	20	30	100	
	Pressure (mm.)	22·0	20·9	20·0	19·5	17·8	
	v (l. g.-mol.$^{-1}$. min.$^{-1}$)	—	26	26	24	14	

The trend in *v* is probably due to condensation of the product molecule and to consecutive, simultaneous, and reverse processes taking place. In order to compare the rate under different conditions the observed values of *v* were extrapolated to zero conversion. The velocity coefficients v_0 so obtained are given in Table II where (*p*) denotes a packed and (*e*) an empty vessel. The packed vessels were filled with tubes of "Pyrex" glass, thereby providing a surface-volume ratio 5 times greater than in the empty vessels. The statement that the formation of gaseous (c) is heterogeneous is based on the observation that the v_0 values in packed vessels are larger than in empty vessels and that v_0 decreases with increasing temperature. A negative temperature coefficient is found also in many other heterogeneous gas reactions.—THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON. [*Received, March 7th*, 1946.]

TABLE II.

	Initial press. (mm.).				Initial press. (mm.).		
Temp.	$C_6H_4O_2$.	C_5H_6.	v_0.	Temp.	$C_6H_4O_2$.	C_5H_6.	v_0.
125°	8·5	13·5	400 (*p*)	145°	11·2	11·2	44 (*e*)
	8·6	11·8	100 (*e*)	153	10·7	11·1	28 (*e*)
	5·9	8·7	100 (*e*)	153	10·7	11·1	40 (*p*)
136	10·0	9·9	60 (*e*)	155	9·6	11·4	30 (*e*)

Metal Sulphide Catalysis of a Simple Cracking Reaction. By B. S. KHAMABATA and ALBERT WASSERMANN.

THESE experiments deal with the reverse diene synthesis: di*cyclo*pentadiene = 2 *cyclo*pentadiene, in which the rupture of the carbon–carbon bonds is accompanied by a rearrangement of double bonds without a release or uptake of hydrogen. We have found that on addition of certain metal sulphides a heterogeneous reaction is superimposed upon the unimolecular homogeneous decomposition of di*cyclo*pentadiene, the kinetics of which we have already studied (*J.*, 1939, 375). The present measurements were all done with 25 c.c. of 0·75M-di*cyclo*pentadiene in paraffin, at 155° and at atmospheric pressure, the activities of the contact substances being characterised by first-order catalytic initial velocity coefficients, V_c, which were obtained from $V_c = V_c' - k_0'$, where k_0' is the unimolecular initial rate constant of the homogeneous reaction and V_c' is the overall initial rate coefficient. The V_c values in the accompanying table all relate to 0·6 g. of contact material, not to unit surface area; these coefficients are merely used as a convenient comparative measure of the catalytic activity of the various sulphides, but there is no experimental evidence to show that the heterogeneous decomposition of di*cyclo*pentadiene is a first-order reaction.

It may be noted that, out of 14 black or brown sulphides, only one had no measurable catalytic effect, whereas all the yellow and white sulphides were inactive; but further work is required before this dependence on colour can be regarded as anything more than fortuitous within the range of sulphides investigated.

Influence of metal sulphides on the rate of decomposition of dicyclopentadiene.

(Solvent, paraffin; temperature, 155°; initial concn. of $C_{10}H_{12}$ = 0·75 g.-mol./l.)

Contact material.	$V_c \times 10^3$ (min.$^{-1}$).	Contact material.	$V_c \times 10^3$ (min.$^{-1}$).
CuS (comml.)	9	NiS	8
CuS (specially prepd.*)	4—7	SnS	8
CuS + 20% $CuSO_4,5H_2O$	5	Tl_2S	4
CuS + 20—60% S	5—6	PbS	7
CuS (pptd. on surface of animal charcoal †)	6	HgS	7
CuS (pptd. on surface of $CaCO_3$ †)	9	Bi_2S_3	5
Cu_2S	5	MoS_2	<0·3
Pyrites	2	ZnS	
FeS	8	SnS_2	
Copper pyrites	5	As_2S_3	
Potassium ferric sulphide	4	SrS	
Ag_2S	2	CdS	

* See below, Nos. 1—6.

† Animal charcoal and calcium carbonate alone are without measurable activity.

Under the experimental conditions k_0' is $2{\cdot}0 \pm 0{\cdot}1 \times 10^{-3}$ min.$^{-1}$, and comparison with the tabulated V_c values shows that with the catalytically active sulphides the initial rate of the cracking reaction is increased by 100—350%.

Experimental.—Di*cyclo*pentadiene was purified as before (*loc. cit.*) and the paraffin was from the stock previously used. All the present measurements were done by the " second method " (*loc. cit.*, p. 379), the dimensions of the apparatus (*ibid.*, p. 380), stirring speed, and temperature of the gas burette being unaltered. The course of a typical experiment with and without a catalyst was as follows :

	Time (mins.)	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
C_5H_6, c.c., collected at 750 mm. pressure	With 0·6 g. of comml. CuS	5·2	9·0	12·2	15·2	17·8	19·6	21·6	23·2	24·6	26·0
	Without catalyst	2·0	3·8	5·2	6·4	7·6	8·6	9·4	10·2	11·0	11·6

In control experiments in which the contact materials without di*cyclo*pentadiene were stirred in paraffin suspension, no detectable gas evolution occurred.

The various cupric sulphide preparations referred to in the table ($V_c \times 10^3 = 4 - 7$ min.$^{-1}$) were made as follows : (1) Hydrogen sulphide was bubbled at room temperature through a 0·9M-cupric sulphate solution which was 0·1M with respect to hydrochloric acid; when all the copper was precipitated, the sulphide was centrifuged off, washed with water, and dried for 8 hours at 90° in air. (2) This was precipitated as sample (1), but the drying was done in a vacuum at room temperature; the dried sample was exposed at room temperature for 70 hours to air. (3) This was precipitated as sample (1), but was washed on the centrifuge with dilute acetic acid, saturated with hydrogen sulphide; the drying was done at room temperature in a vacuum. (4) This was precipitated as sample (3), but the cupric sulphate solution did not contain hydrochloric acid. (5) This was precipitated by slowly adding a 0·2M-sodium sulphide solution to an equivalent volume of 0·2M-cupric sulphate, the precipitate being washed and dried as sample (3). (6) This was prepared as sample (3) except that water was used for the washing.

The mixtures of cupric sulphide with cupric sulphate or sulphur were made by using sample (2), the dry components being ground together. The cupric sulphide–animal charcoal and the cupric sulphide–calcium carbonate catalysts were made as follows : 10 G. of animal charcoal (A.R.) or 10 g. of finely powdered calcium carbonate were stirred, at room temperature, for 45 mins. with 120 c.c. of 0·8M-cupric sulphate solution which was 1M with respect to hydrochloric acid; hydrogen sulphide was then passed through the suspension for ½ hour, and the mixture filtered, the residue being dried under the same conditions as sample (1).

The ferrous sulphide was made by precipitating a 0·1M-ferrous sulphate solution with an equivalent quantity of 0·1M-ammonium sulphide; the precipitate was washed with dilute acetic acid saturated with hydrogen sulphide, and dehydrated by heating to 120° under a layer of paraffin. The suspension of the sulphide in paraffin was added to the di*cyclo*pentadiene after an aliquot portion of the suspension had been analysed.

The other sulphides were all finely powdered, passed through a 50-mesh sieve, and dried in a vacuum at room temperature to constant weight.

No attempt was made to investigate the influence of temperature or concentration of di*cyclo*pentadiene on the rate of the catalysed decomposition, the accuracy of the V_c values being only ±15%. A few tests were made, however, in which the weight of the catalyst was varied while everything else was kept constant : V_c increased in all cases with increasing weight of sulphide; *e.g.*, with 0·2, 0·6, and 3·6 g. of a commercial cupric sulphide the V_c values were respectively 5×10^{-3}, 9×10^{-3}, and 35×10^{-3} min.$^{-1}$.—THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON. [*Received, March* 22*nd*, 1946.]
