#### NOTES

Chloro-substituted Alkenyl Dithiocarbamates										
	R = C	$H_2CH=CC1CH_3$ ,	$R' = CH_2$	CC1=CH2, R"	$= CH_{2}$	2CH==C	CHC1			
Derivatives	Vield. % crude	B.p., °C., 1 mm. or m.p.	n 28 D	Empirical formula	Nitr Caled.	ogen Found	Sul Calcd.	fur Found	Chlo Caled.	Found
(CH <sub>3</sub> ) <sub>2</sub> NCSSR	87.5	27-28°		$C_7H_{12}CINS_2$	6.68	6.90	30.57	30.60	16.90	17.00
(CH <sub>3</sub> ) <sub>2</sub> NCSSR′	88.1	35-37*		$C_6H_{10}CINS_2$	7.16	7.34	32.76	32.80	18.11	18.07
(CH <sub>3</sub> ) <sub>2</sub> NCSSR″	94.5	Dec. <sup>b</sup>	1.6135	C6H10CINS2	7.16	7.04	32.76	32.60	18.11	18.05
$(C_2H_5)_2NCSSR$	84.4	$158-160^{b}(2 \text{ mm.})$	1.5800	C <sub>9</sub> H <sub>16</sub> C1NS <sub>2</sub>	5.89	5.82	26.96	26.86	14.91	14.65
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCSSR'	89.0	128–130 <sup>b</sup>	1.5822	C <sub>8</sub> H <sub>14</sub> C1NS <sub>2</sub>	6.26	6.18	28.65	28.57	15.84	15.74
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCSSR"	85.0	Dec. <sup>b</sup>	1.5891	C <sub>8</sub> H <sub>14</sub> C1NS <sub>2</sub>	6.26	6.22	28.65	28.41	15.84	15.84
H2NCSSR	83.0	25-27°		$C_5H_8C1NS_2$	7.71	7.93	35.29	34.96	19.51	19.84
$(CH_2 = CHCH_2)_2 NCSSR$	95.1	Dec. <sup>b</sup>	1.5881	$C_{11}H_{16}C1NS_2$	5.35	5.50	24.49	24.42	13.54	13.33
(CH2=CHCH2)2NCSSR'	82.9	$145 - 146^{b}$	1.5882	$C_{10}H_{14}C1NS_2$	5.65	5.39	25.87	26.00	14.31	14.60
C4H8NO—CSSR"	91.8	$-10^{a}$	1.6261	C <sub>8</sub> H <sub>12</sub> C1NOS <sub>2</sub>	5.89	5.91	26.97	27.22	14.91	15.20
C4H8NO—CSSR°	95.5	56-57°		$C_9H_{14}C1NOS_2$	5.56	5.71	25.46	25.56	14.08	14.04
C4H8NO-CSSR"	95.0	73–74°		C <sub>8</sub> H <sub>12</sub> C1NOS <sub>2</sub>	5.89	6.06	26.97	26.90	14.91	15.29
$C_6H_{12}N_2$ (CSSR') <sub>2</sub> <sup>d</sup>	97.0	124–125°		$C_{14}H_{20}Cl_2N_2S_4$	6.74	6.76	30.87	31.30	17.07	16.69
$C_6H_{12}N_2$ (CSSR) <sub>2</sub> <sup>d</sup>	95.0	102-103°		$C_{16}H_{24}Cl_2N_2S_4$	6.32	6.33	28.91	28.88	15.99	15.59
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NCSSR	91.7	Dec. <sup>b</sup>		$C_9H_{16}C1NO_2S_2$	5.19	5.17	23.77	23.36	13.14	12.90
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NCSSR′	93.4	Dec. <sup>b</sup>		$C_8H_{14}C1NO_2S_2$	5.48	5.23	25.07	25.27	13.86	13.68
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NCSSR"	87.8	Dec. <sup>b</sup>	• • • •	$C_8H_{14}C1NO_2S_2$	5.48	5.47	25.07	24.83	13.86	13.45
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TABLE I

<sup>a</sup> M.p. <sup>b</sup> B.p. <sup>c</sup> C<sub>4</sub>H<sub>8</sub>NO = morphinyl. <sup>d</sup> C<sub>6</sub>H<sub>12</sub>N<sub>2</sub> = 2,5-dimethylpiperazine group. <sup>e</sup> M.p. recrystallization from ethyl alcohol.

dithiocarbamate, sodium diallyldithiocarbamate, ammonium dithiocarbamate, sodium 4-morpholinecarbodithioic acid, sodium bis-(2-hydroxyethyl)dithiocarbamate, or disodium 2,5-dimethyl-1,4piperazinedicarbodithioate with the following unsaturated chloro compounds: 1,3-dichloro-2-butene, 2,3-dichloro-1-propene and 1,3-dichloropropene. The reaction may be represented as follows: RSNa + R'Cl  $\rightarrow$  ŘSR' + NaCl where R is a thiocarbamyl group and R' is a chloro-substituted alkenyl group. Reaction of sodium 3-chloro-2-butenyl trithiocarbonate dihydrate with N,Ndiethylthiocarbamyl chloride did not yield the expected product, 3-chloro-2-butenyl N,N-diethylthiocarbamyl trithiocarbonate but gave instead 3-chloro-2-butenyl diethyldithiocarbamate. The former presumably was unstable, decomposing to form the latter and carbon disulfide. The reaction may be represented as

# $(C_2H_5)_2NCSSCH_2CH=CC1CH_2 + CS_2$

Physical data are listed in Table I.

#### Experimental<sup>8</sup>

Chloro-substituted Alkenyl Dithiocarbamates. General Procedure.—To one mole of 15-27% aqueous solution of sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate, sodium bis-(2-hydroxyethyl)-dithiocarbamate, ammonium dithiocarbamate, sodium 4-morpholinecarbodithioic acid, sodium diallyldithiocarbamate and (0.5 mole) of disodium 2,5-dimethyl-1,4-piperazine dicarbodithioate containing a few drops of dodecylbenzene sulfonate was added one mole of either 1,3-dichloro-2-butene, 2,3-dichloro-1-propene or 1,3-dichloropropene.<sup>10</sup> An exothermic reac-

(8) All melting points were taken upon a Fisher-Johns block and are uncorrected.

(9) Kindly supplied by E. I. du Pont de Nemours and Company. Wilmington, Delaware.

(10) Kindly supplied by Shell Chemicals Corporation, Emeryville. California.

tion set in, the temperature rising 5-16° over a period of 20 minutes. The reaction mixture was stirred for six hours. For compounds possessing a melting point below 56° the organic layer was dissolved in 400 ml. of ethyl ether, the ether solution washed with water until the washings were neutral to litmus, dried over sodium sulfate and the solvent removed *in vacuo*. For compounds melting above 55°, the solid was recovered by filtration, washed with water until the wash water was neutral to litmus and air-dried at room temperature.

3-Chloro-2-butenyl Diethyldithiocarbamate. Alternate Method.—To an agitated suspension of 80 g. (0.31 mole) of sodium 3-chloro-2-butenyl trithiocarbamate dihydrate in 500 ml. of acetone, was added a solution containing 47.5 g. (0.31 mole) of N,N-diethylthiocarbamyl chloride<sup>11</sup> in 300 ml. of acetone. An exothermic reaction set in, the temperature rising from 21 to 29° within 20 minutes. The reaction mixture was stirred for one day. The sodium chloride was removed by filtration, the acetone recovered by distillation and the residue dried over sodium sulfate. A yield of 65 g. (88.6%) of an amber oily product was obtained.

Anal. Caled. for  $C_0H_{16}ClNS_2$ : Cl, 14.91; N, 5.89. Found: Cl, 15.03; N, 5.71.

Acknowledgment.—Grateful acknowledgment is made for the analyses rendered by Mr. Edward Null and to the Monsanto Chemical Company for permission to publish this work.

(11) Kindly supplied by Sharples Chemicals Inc., Philadelphia, Pennsylvania.

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Vanadium Oxide Hydrogenation Catalyst. IV.<sup>1</sup> The Action of Vanadium Oxide Catalyst on Cyclohexene

> By V. I. Komarewsky and T. A. Erikson Received April 2, 1953

The work presented in this article has been undertaken in order to find additional information of the difference in mechanism between metal and

(1) For paper III of this series see V. I. Komarewsky and B. A. Knaggs, Ind. Eng. Chem., 43, 1414 (1951).

metal oxide catalysts in vapor phase hydrogenation and dehydrogenation reactions. It is known that cycloölefins undergo a complete hydrogen disproportionation to cycloparaffins and aromatics on the surface of metal catalysts (*i.e.*, platinum, palladium and nickel).

In the present work, cyclohexene was subject to the action of pure vanadium trioxide at temperatures of  $250-450^{\circ}$  in an atmosphere of hydrogen and of nitrogen. The obtained results were compared with theoretical calculations.

Theoretical equilibrium concentrations of benzene and cyclohexane as a function of temperature were calculated from the equilibrium constants as presented by Rossini,<sup>2</sup> et al. Benzene and cyclohexane would be expected to form by one or more of three reactions, namely, hydrogenation, dehydrogenation or disproportionation. Figure 1 presents the theoretical concentrations of products from these reactions together with the experimental results. The theoretical concentrations were calculated on the basis of the initial partial pressure of cyclohexene being 0.12 atmosphere to that of hydrogen being 0.88 atmosphere, as used in this experimentation. It can be seen from Fig. 1 that, theoretically, hydrogenation would be the major reaction below 250°, both hydrogenation and dehydrogenation in temperature range 250-300° and dehydrogenation above 300°. The disproportionation reaction is possible throughout these temperatures. The experimental results have shown that cyclohexene in the presence of hydrogen, when passed at various temperatures  $(250-450^{\circ})$  over vanadium trioxide catalyst, shows no hydrogen disproportionation, but direct hydrogenation and dehydrogenation reactions approaching the theoretical values.

This fact is in line with the interpretation of edgewise adsorption of the organic molecule on the surface of metal oxide catalysts *versus* flat adsorption on the surface of metals.

### Experimental Part

Cyclohexene (Eastman Kodak Co.) b.p.  $82.5-83.5^{\circ}$ ,  $n^{20}D$  1.4468, was vaporized in the stream of hydrogen at a constant rate into a glass tube filled with catalyst and placed in an electrically heated oven. The constancy of cyclohexene/hydrogen ratio (0.12:0.88 atmosphere) was maintained by a flowmeter (for hydrogen) and temperature of the evaporator (for cyclohexene). The liquid hourly space velocity was maintained between 0.015-0.017. The products were collected in receivers cooled with water and Dry Ice. Analysis was by distillation, chromatographic adsorption (silica gel) and determination of physical constants. The catalyst was prepared and activated as before.<sup>1</sup>

The experimental results are presented in Table I. It can be seen from the results obtained at lower temperatures that the activity of vanadium trioxide is extremely low. This was to be expected, since in the earlier work<sup>3</sup> with the same catalyst on hydrogenation of olefins its activity was at its maximum at higher temperatures (around  $400^{\circ}$ ), which goes parallel with hydrogen adsorption and the amount of vanadium trioxide present. At higher temperatures the catalyst exhibits high activities and the reaction of dehydrogenation to benzene approaches the theoretical values. It is of importance for this discussion that in no case was there an excessive formation of cyclohexane and this consequently indi-

(2) M. B. Epstein, K. S. Pitzer and F. D. Rossini, J. Research Natl. Bur. Standards, 42, 379 (1949).

(3) V. I. Komarewsky and J. R. Coley, THIS JOURNAL, 70, 4163 (1948).



Fig. 1.—Reaction of cyclohexene and hydrogen. Theoretical equilibrium concentrations (solid lines) and experimental results (dotted line) over vanadia catalyst.

cates there is no hydrogen disproportionation reaction. Experiments carried out in an atmosphere of nitrogen showed similar results, the per cent. of dehydrogenation being somewhat higher than in experiments in hydrogen.

#### TABLE I

REACTION OF CYCLOHEXENE IN THE PRESENCE OF HYDRO-GEN AND OF NITROGEN (1:8 RATIO) OVER VANADIUM TRI-OXIDE CATALYST. LIQUID HOURLY SPACE VELOCITY 0.015-0.017

<sup>тетр.,</sup> °С.	n <sup>20</sup> D of the product	Chromatographic analysis <sup>a</sup> of the product (%) CeH10 CeH0 CeJ				
	A. Hy	drogen expe	riments			
<b>25</b> 0	1.4465	98.5	1.5	0.5		
300	1.4471	91.5	5.0	3.5		
350	1.4583	53.8	38.5	7.7		
400	1.4886	11.0	81.0	8.0		
450	1.5010	0.0	97.0	3.0		
	B. N	itrogen expe	riments			
300	1.4473	100.0	0.0	0.0		
350	1.4538	44.5	55.0	>0.5		
400	1.4730	15.5	84.0	>0.5		

<sup>a</sup> Initial boiling point of all products was 80° which clearly indicated that no isomerization to methylcyclopentane or methylcyclopentene took place.

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### The Reaction between Periodate and Cobaltous Ions<sup>1</sup>

# By Ralph E. Jentoft and Rex J. Robinson<sup>2</sup>

## **Received March 23, 1953**

During a study of the determination of potassium as the metaperiodate, chemical evidence was obtained which indicated an oxidation-reduction reaction between periodic acid and divalent cobalt as a function of the hydrogen ion concentration. This reaction does not appear to be clearly indicated in the literature. Gmelin's "Handbuch"<sup>8</sup> leaves the matter an open question in citing two papers with

(1) This work was partly supported by the Office of Naval Research under Contract No. N8onr-520/III with the University of Washington.

(2) Correspondence should be addressed to Rex J. Robinson.

(3) "Gmeliñs Handbuch der anorganischen Chemie," No. 58 Cobalt, Part A, Sect. 2, 8th ed., Verlag Chemie G.m.b.h., Berlin, 1932, p. 317.

