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DETERMINATION OF DITHIOCARBAZATES, STOICHIOMETRIC COMPOSITION AND HEAT OF FORMATION OF ITS METHALIC COMPLEXES BY THERMOMETRIC TITRATION

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ABSTRACT

An automatic thermometric titration technique was applied to the determination of xanthate in methanolic medium with a methanolic solution of iodine. Thermograms with sharp arrest points were obtained, from which the reaction heat was measured. The thermometric method was also applied to the determination of dithiocarbazates, the stoichiometry of their complexes with methalic ions and their reaction heats.

INTRODUCTION

Dithiocarbazates have been used as analytical reagents and substitutes of dithiocarbamates as fungicide products and accelerators of vulcanization [1–7], but no method has been devised for their titration. Like dithiocarbamates, they are decomposed by mineral acids to yield carbon disulphide and hydrazine. Carbon disulphide can then be gathered and determined iodometrically or spectrophotometrically. Clarke et al. [8] reported a method for the determination of dithiocarbamates based on their decomposition in acid medium, the carbon disulphide produced being gathered on alcoholic potassium hydroxide and determined iodometrically using starch as indicator. In this paper we report the study of the iodometric enthalpimetric titration in alcoholic medium of carbon disulphide previously converted into xanthate, and determination of the enthalpy of this reaction. The method was applied to the determination of dithiocarbazates after their decomposition by acids. The thermometric method has also been used to find the stoichiometry of the precipitates formed by dithiocarbazates in the presence of certain methalic ions.

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EXPERIMENTAL

Reagents

Potassium hydroxide, 0.5 M in methanol, was used to absorb carbon disulphide.

Carbon disulfide 0.05 M stock solution: 3.8 g of carbon disulphide (Merck) were dissolved in 1 l of methanol. It was standardized by conversion to xanthate with potassium hydroxide in methanol and both titration with iodine using starch as indicator and potentiometric titration with a methanolic solution of iodine. It was stored in a refrigerator at 0°C.

Iodine: 0.5 and 0.1 M solutions in methanol, standardized against As_2O_3 [9].

Potassium phenyldithiocarbazate was prepared according to Anthoni et al. [10] by addition of carbon disulphide to phenylhydrazine in alkaline medium (m.p. 144–146°C). The elemental analysis results were as follows: calculated for $K[(C_6H_5)NHNHCS_2]\cdot 2H_2O$: C, 32.55; H, 4.26; N, 10.84; S, 24.82%; found: C, 32.84; H, 4.21; N, 10.45; S, 24.95%.

Phenyldithiocarbazates of methalic ions were prepared by dropwise addition and with moderate stirring of a 1 M aqueous solution of the methalic ion to a 0.1 M aqueous solution of the reagent. The precipitate formed was filtered, washed with distilled water and vacuum dried.

The purity was determined from elemental analysis data.

APPARATUS

The temperature was measured with a fast-response thermistor and Wheatstone bridge system using the electrical circuit proposed by Lumbiarres et al. [11]. The thermistor resistance was 11.95 kΩ at 20°C, the temperature used throughout.

The bridge parameters were calculated to give a linear response to temperature changes in the range used, and to be compatible with a chart-recorder of 1 MΩ input impedance.

The titration assembly (Fig. 1) consisted of 100-ml Dewar covered by a 2 cm thick block of expanded polyurethane and placed in another silvered Dewar. The thermistor, the burette tip and the heater (R_c) were fixed to the lid, and the solution was stirred by a paddle rotating at 600 rpm. The titrant was delivered at constant rate (0.142 ml min^{-1}) by a 2.5-ml automatic burette (Radiometer model ABU 12). Less than 1 ml of titrant was used in each titration in order to minimize heat capacity variations in the system.

A Yokogawa chart recorder (model 4.701), with different paper speeds and sensitivities (100–0.5 mV) was used. The sensitivity of the bridge was fixed at a constant value of 5 mV K^{-1} at 20°C.

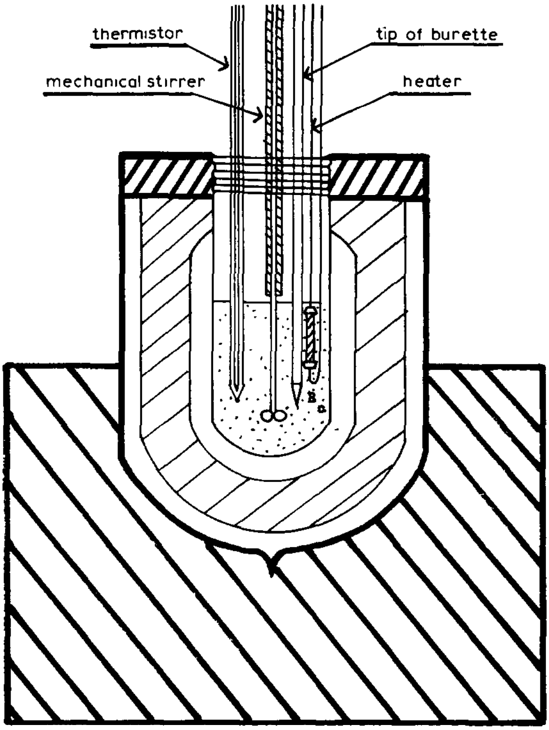

Fig. 1. Adiabatic titration unit.

A Beckman Acta M-VII double-beam spectrophotometer with an automatic register equipped with 10-mm cells was used for recording spectra in the UV and visible regions. The scanning speed was 2 nm s^{-1}.

PROCEDURES

Xanthate determination

A solution (40 ml) of xanthate, prepared by mixing an aliquot of the methanolic solution of carbon disulphide with a solution of sodium hydroxide in methanol, was placed in the titration cell, slightly acidified with 30% acetic acid, and titrated thermometrically with 0.5 M iodine in methanol. After temperature equilibration, the baseline was recorded for 10 min before the titration was started. Titrant was added at 0.142 ml min^{-1} until well past the end point (to find the heat of dilution of the system) and recording was stopped some minutes later (to give the cooling rate). The end point was given by intersection of the dilution line and the reaction-period line. Figure

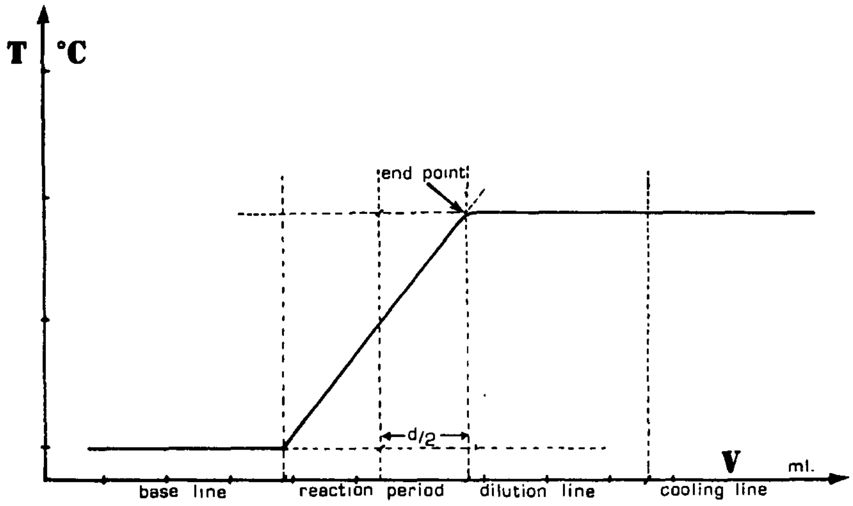

Fig. 2. Typical thermometric titration.

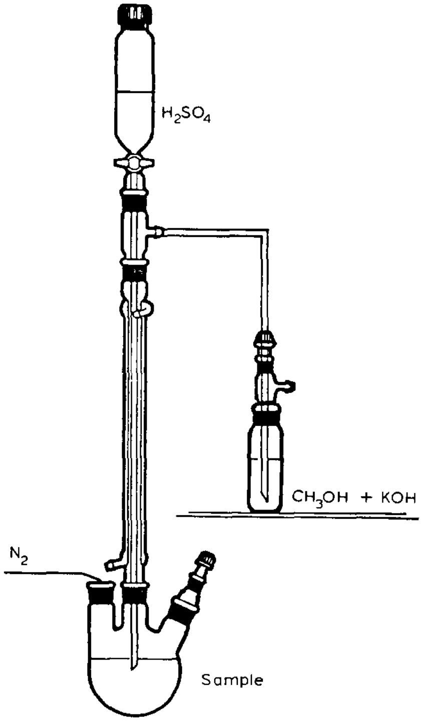

Fig. 3. Device used for the determination of dithiocarbazates.

2 shows a typical titration curve. The temperature increase was determined according to Barthel's method [12].

Determination of dithiocarbazates (Fig. 3)

An accurately weighed sample, equivalent to 5–17.5 mg of carbon disulphide, was placed in a flask provided with an air refrigerant and a trap containing 20 ml of KOH methanolic solution, then 50 ml of hot sulphuric acid (1 : 1) were added to the reaction container. The carbon disulphide produced was drawn into the trap with a current of nitrogen at a flow rate of 20 ml min^{-1}. After 10 min the contents of the trap were passed to the Dewar with 20 ml of methanol and titrated by the above method.

Determination of reaction enthalpy

The enthalpy of reaction can be found from the temperature change by determination of the enthalpimetric constant of the cell [13,14], by use of electrical heating or by means of a calibration curve with a reaction of known enthalpy change [15].

In this paper we used both the electrical calibration and calorific capacity methods. We did not use the method based on a known value of enthalpy of reaction because there was no such reaction suitable.

The electrical calibration method was performed using the circuit reported by Lumbiarres et al. [11] and described in a previous paper [16]. The ΔH value was determined by the slope method, in which the slope of the titration curve is compared with the slope of the curve of the thermogram, obtained by pasing an electrical current through the electric heater, adjusted to be almost the same as the titration thermogram, and application of the equation of Tyson et al. [17]:

$$\Delta H = \frac{E_c E_p S_1}{4.185 R_p N F S_2}$$

were E_c and E_p are the voltage drops across the standard resistor and the calibration heater, S_1 and S_2 are slopes of the chemical and electrical titrations, respectively, F is the rate of titrant addition (ml s^{-1}), and N is the normality of the titrant.

The electrical calibration method was used with the circuit shown in Fig. 4. The steady power source (SPS) was regulated between 1.5 and 11.5 V with a maximum output current of 600 mA. The ballast resistor R_{ex} and heating resistance R_c were both 9.8 Ω and R_c was varnished for protection against the reagents and to avoid electrical losses. The standard resistor R_p (9.303 Ω at 19°C) was made of constantan wire coiled on bakelite and immersed in a glycerine bath for easy dissipation of heat. Both potentials, across the calibration resistance and the standard resistance, were measured with a

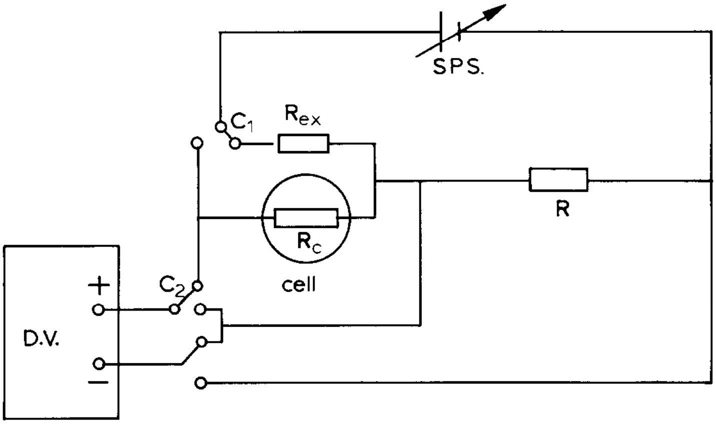

Fig. 4. Schematic calibration circuit.

digital voltmeter (DV, Sinclair Multimeter model PDM-35). The accuracy of the method was contrasted by application to the titration of potassium chloride with a silver nitrate and comparison of the value obtained with that found in the literature (value obtained 15.60 ± 0.2 kcal mol^{-1}, value found in the literature 15.70 ± 0.2 kcal mol^{-1}).

The method of calorific capacity is based on the measurement of the overall temperature variation (determined from the enthalpigram) produced during the titration of N_m moles of compounds and application of the equation:

$$\Delta H \frac{Q}{N_m} = \frac{\Delta TC}{N_m}$$

The calorific capacity of the cell and its contents was determined under the same experimental conditions by dissipating a known amount of heat by Joule's effect using the mentioned electric circuit. The mean value of 14 determinations of calorific capacity obtained in a methanolic medium was 0.0303 ± 0.002 kcal $°C^{-1}$, and that obtained in an aqueous medium was 0.0576 ± 0.0008 kcal $°C^{-1}$.

RESULTS AND CONCLUSIONS

The stability of 9.5×10^{-3} and 1.9×10^{-3} M solutions of xanthate in methanolic media at 20°C, determined by measuring the absorbance at 383 nm which is the λ_{max} of the spectrum in methanol (Fig. 5), showed a 2 and 4% decomposition after 2 h in neutral medium whereas in basic media they remained practically stable for more than 8 h (Table 1). Weak acidification of the solution immediately before titration is recommended. The reaction of

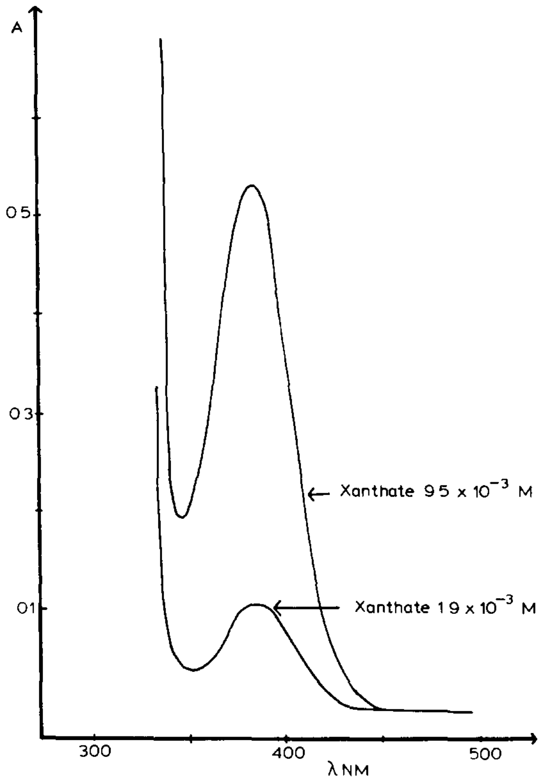

Fig. 5. Absorption spectrum of xanthate in methanolic medium.

TABLE 1

Variation of the absorbance at 383 nm of a solution of xanthate with time

Time (h)	9.5×10^{-3} M Absorbance	Percentage decomposition	1.9×10^{-3} M Absorbance	Percentage decomposition
Neutral medium				
0	0.535	0	0.106	0
2	0.525	1.9	0.102	3.8
4	0.518	3.2	0.099	6.6
6	0.510	4.7	0.098	7.5
8	0.507	5.2	0.094	11.3
10	0.505	7.6	0.091	14.1
Basic media				
0	0.538		0.107	
0.5	0.539		0.108	
2.5	0.537		0.107	
4.5	0.540		0.107	
6.5	0.540		0.108	
8.5	0.539		0.107	

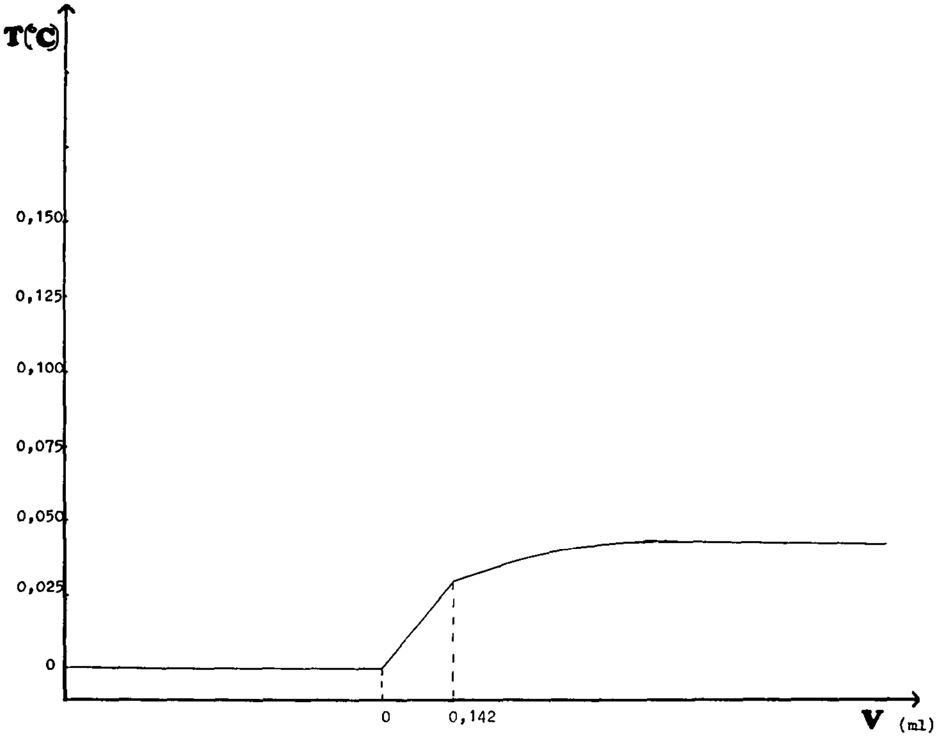

Fig. 6. Enthalpigram of the titration of 5.4 mg xanthate with 0.5 M I_2.

carbon disulphide with methanolic potassium hydroxide and formation of xanthate was quantitative and almost instantaneous under the conditions used. The enthalpigrams were linear and allowed easy detection of the end point.

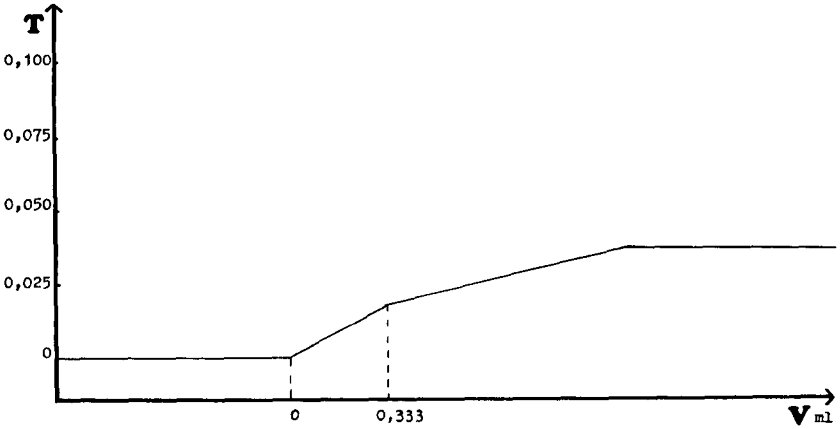

Fig. 7. Enthalpigram of the titration of 2.7 mg xanthate with 0.1 M I_2.

TABLE 2

(A) Data obtained in the calculation of the enthalpy of reaction by the electrical method

Sample	Xanthate (mmol)	E_p	E_c	Solution temperature (°C)	ΔH (kcal mol^{-1})
1	0.363	0.742	0.775	20.11	−26.48
2	0.376	0.708	0.726	19.33	−26.85
3	0.336	0.706	0.725	20.60	−26.30
4	0.345	0.708	0.724	19.70	−26.84
5	0.386	0.710	0.723	19.97	−26.80
6	0.363	0.713	0.720	19.50	−26.61
7	0.359	0.712	0.719	19.50	−26.11
8	0.327	0.711	0.718	19.60	−25.95
9	0.335	0.712	0.720	19.92	−26.28
10	0.364	0.712	0.720	19.87	−26.89
					$\bar{X} = -26.51$
					$\sigma = 0.34$

(B) Data obtained in the calculation of the enthalpy of reaction by the method of calorific capacity of the titration cell

ΔT (°C)	Amount of sample (mmol)	ΔH (kcal mol^{-1})	ΔT (°C)	Amount of sample (mmol)	ΔH (kcal mol^{-1})
0.157	0.177	−26.88	0.166	0.188	−26.75
0.153	0.172	−26.95	0.146	0.168	−26.33
0.129	0.149	−26.23	0.151	0.172	−26.60
0.129	0.148	−26.41	0.167	0.193	−26.22
0.154	0.177	−26.36	0.151	0.171	−26.76
					$\bar{X} = -26.55$
					$\sigma = 0.27$

The lowest concentration limit of CS_2 for a useful analytical titration is determined by the molarity of the titrant and temperature change obtained at the end point.

Our results show that with a 0.5 M iodine solution 0.0710 mmol (5.40 mg) of carbon disulphide can be determined with an error lower than 1% and a relative standard deviation of 0.28% (Fig. 6). Using 0.1 M iodine, 0.035 mmol (2.7 mg) can be determined with a relative standard deviation of 0.3% (Fig. 7).

Table 2 gives the reaction heat corresponding to ten determinations, mean value and standard deviation determined by both procedures. The results show that values obtained by both methods were significantly similar.

Table 3 gives the results obtained for the methalic dithiocarbazates. Dithiocarbazates were placed in the digestion flask, 50 ml of (1 : 1) sulphuric acid added, and heated slightly.

TABLE 3

Thermometric titration of dithiocarbazates

Compound	Mass of substance (g)	Amount of substance in 40 ml (mmol)	CS_2 (mmol)		Error (%)
			theor.	found	
FDTCK·H_2O	0.0211	0.0817	0.0817	0.0810	−0.8
	0.0180	0.0698	0.0698	0.0691	−1.0
	0.0164	0.0635	0.0635	0.0630	−0.8
$(FDTC)_2Zn$	0.0160	0.0373	0.0745	0.0740	−0.7
	0.0152	0.0353	0.0706	0.0708	0.3
	0.0153	0.0355	0.0710	0.0704	−0.8
$(FDTC)_2Ni$	0.0193	0.0455	0.0910	0.0902	−0.8
	0.0192	0.0452	0.0904	0.0900	−0.4
	0.0184	0.0434	0.0868	0.0870	0.2
$(FDTC)_2Cd$	0.0128	0.0268	0.0537	0.0531	−1.1
	0.0155	0.0323	0.0647	0.0650	0.5
	0.0152	0.0318	0.0637	0.0641	0.6
$(FDTC)_2Cu$	0.0191	0.0444	0.0888	0.0884	−0.4
	0.0188	0.0439	0.0877	0.0875	−0.2
	0.0192	0.0447	0.0894	0.0889	−0.5

Finally, the thermometric method was used to determine the composition of the precipitates formed by potassium phenyldithiocarbazate and Cd(II), Ni(II), Zn(II) and Cu(II) ions. Reaction enthalpies were determined from the enthalpigrams using both the electric and calorific capacity methods. Results are given in Table 4. Precipitate compositions found are in complete agreement with those obtained by elemental analyses. With Cu(II) a

TABLE 4

Cation	Reagent : cation stoichiometry	No. of determinations	Method [a]	ΔH at 20°C (kcal mol^{-1})
Cd(II)	2:1	4	CE	-25.45 ± 0.54
		4	CC	-25.53 ± 0.22
Ni(II)	2:1	4	CE	-11.55 ± 0.27
		6	CC	-11.58 ± 0.14
Zn(II)	2:1	4	CE	-7.90 ± 0.57
		4	CC	-7.98 ± 0.41
Cu(II)	1.75:1	6	CE	-27.89 ± 0.37
		8	CC	-27.94 ± 0.30

[a] CE, electrical method; CC, calorific capacity.

stoichiometry of 1.75 : 1 was found, which could be due to oxidation of the reagent.

The IR study of these precipitates confirms a structure in which the coordination of the methalic ions occurs through sulphur atoms, according to the reports of Battistoni et al. [18].

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