875. *The Reaction between Aromatic Compounds and Derivatives of Tertiary Acids. Part VIII.* The Use of an Infrared Gas Analyser for the Quantitative Determination of Carbon Monoxide.*

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A commercial " Infra-Red Gas Analyser " has been employed to measure the rate of evolution of carbon monoxide arising from the decomposition of pivaloyl chloride by aluminium chloride. The method is more accurate than the titration procedure used earlier,[1] and more flexible, facilitating rapid and consistent measurements on a much wider range of concentrations.

PIVALOYL CHLORIDE is decomposed by aluminium chloride to carbon monoxide and *iso*butene, or if an aromatic hydrocarbon is present, a *tert.*-butyl derivative. The rate of this reaction was measured by Rothstein and Saville [1] who titrated the unchanged acid obtained from samples withdrawn from the reaction mixture. The order with respect to the aromatic component was zero and, since the concentration of catalyst remained constant, the reaction afforded a first-order constant of approximately 0·043 min.$^{-1}$ for unit concentration of the aluminium chloride.

The above procedure measures the rate at which carbon monoxide is eliminated only in specially chosen, favourable conditions. The inferences drawn by Rothstein and Saville were valid because it had been ascertained previously that the total yield of gas more or less corresponded with the amount of acid chloride initially taken. In general, expulsion of carbon monoxide may be accompanied by reaction of the acid chloride with any aromatic compound present, or in its absence, with the *iso*butene resulting from the decomposition.[2] In such cases, therefore, estimation of unchanged acid is unsuitable except for measurement of the total reaction. There are also other serious disadvantages inherent in the titration method. The large proportion of reaction which occurs before withdrawal of the first sample limits the concentration of catalyst which can be used. On the other hand, too low a concentration of the acid chloride leads to inaccurate titrations. So it is impossible to investigate the faster reactions or those in which the catalyst is in molecular excess. The procedure is in any case tedious and inflexible and it is by no means certain that the reacting complex yields back all the original acid when it is decomposed. Thus it is not feasible to minimize undesirable side-reactions by the use of relatively high concentrations of catalyst and it is likewise found that the reactions of alkylated acetyl chlorides are unmanageably fast even at low concentrations.

The quantitative estimation of carbon monoxide liberated during a reaction has usually been made volumetrically,[3] but in the present case the nature of the reaction to be studied and the large volume of gas evolved suggested that advantageous use could be made of the 3-box Infra-Red Gas Analyser developed in this country by Messrs. Sir Howard Grubb, Parsons and Co. Ltd. This instrument responds, unless overlapping absorption bands are present, to one particular gas and to no other. The variable sensitivity makes it possible to use gaseous mixtures over a wide range of composition whilst the time of response is usually negligibly small.

EXPERIMENTAL

The Infra-Red Gas Analyser was connected to an " Ether " automatic recorder giving a reading every 30 sec. on a 5″ chart graduated horizontally in 100 divisions and vertically at ½″ intervals from which the time could be read off. The smallest reading of the horizontal divisions which could be clearly read was approximately 1/200 of the full scale, the exact reading being dependent on the working conditions. Maximum stability was achieved by switching on the Analyser at least 1 hr. before use. Although a voltage stabiliser was fitted, the mains

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* Part VII, *J.*, 1952, 4136.

[1] Rothstein and Saville, *J.*, 1949, 1954.

[2] Grundy, Hsü, and Rothstein, *J.*, 1952, 4136.

[3] Schierz, *J. Amer. Chem. Soc.*, 1923, **45**, 447; Dittmar, *J. Phys. Chem.*, 1929, **33**, 533.

frequency variations (about 6%) at peak hours caused serious changes in the sensitivity, necessitating frequent checks by means of the calibrating shutter with consequent corrections to the percentages of carbon monoxide read off the chart. In general, the sensitivity could be adjusted during the preliminary calibration so that a full scale reading of the meter was obtained corresponding to the maximum concentration of carbon monoxide likely to be encountered during a determination. Though a constant-temperature room was not used, the large thermal inertia of the instrument counteracted small variations due to temperature changes.

The speed of response of the Analyser is governed by two factors. One is the electrical nature of the circuit, which causes a delay of 8 sec.; however, readings were recorded every ½ min. and therefore this delay was unimportant. Experimental conditions govern the other. For many experiments an absorption tube 30 cm. long with a capacity of 110 c.c. was used in conjunction with a rate of flow of 200 c.c./minute. It is usually considered that the time taken to replace a gas entirely is that taken for the passage of four times its volume, so that in the above example a complete change was obtained in 2 min. For a steady rate of flow the time lag was constant and significant errors were not introduced. For faster reactions where the higher concentrations of carbon monoxide necessitated a shorter path (*i.e.*, a shorter absorption tube of approx. length 10 cm.) a much shorter response time was obtained.

The Analyser was calibrated by passing artificial mixtures of nitrogen and carbon monoxide through the apparatus until steady readings were obtained. A second method duplicated the subsequent experimental conditions and agreed with the first. A measured flow of carbon monoxide was passed into a stream of nitrogen flowing at a known and constant rate into the Analyser, and the steady readings on the chart were plotted against the known composition of the mixture. This method proved to be rapid and accurate and was therefore extensively employed. The flow of nitrogen was determined by a capillary flowmeter with a capacity of 150—250 c.c./min. For carbon monoxide rates below 1 c.c./min. were measured by a mercury-pellet flowmeter; above this figure and below 100 c.c./min. a soap-bubble flowmeter using soap films made from a mixture of 0·5% aqueous " Aerosol " (3 vols.) and glycerol (1 vol.) was found to be convenient.

Nitrogen at constant pressure from a cylinder was passed through a capillary-type flowmeter and washed by concentrated sulphuric acid and then activated alumina. From there the gas passed into four wash-bottles, three of which were immersed in the thermostat. These contained benzene in order to saturate the nitrogen with vapour and to adjust its temperature to that of the reaction mixture. After passing through a condenser, the mixed gases were washed with water and dried by concentrated sulphuric acid which also removed any olefin formed during the reaction, and finally passed through a small tube containing anhydrous calcium chloride and a small cotton wool filter into the Analyser. The bulb of a thermometer was inserted into the stream of issuing gases which were insulated from external heat effects. Before the commencement of an experiment, *i.e.*, before addition of the acid chloride, nitrogen was swept through the apparatus and the zero adjusted to compensate for the small deflection due to benzene (calibration having been carried out under these conditions). The time for the maximum deflection during a reaction was dependent on the rate of flow of nitrogen and on the length of absorption tube used. It varied from 6 to 30 min. and accordingly the exact commencement of the reaction could not be determined from the graph. No serious error was introduced, however, by assuming that the reaction started 30 sec. before the first positive reading on the recorder.

Preparation of Materials and Method of Reaction.—Aluminium chloride was prepared in an electric furnace from aluminium turnings and hydrogen chloride.[4] The product was resublimed in a current of dry hydrogen chloride, then in a stream of dry nitrogen, and finally stored over phosphoric oxide in aluminium-capped bottles. It was a fine, nearly white powder, easily soluble in nitrobenzene. The benzene was sulphur-free and of molecular-weight quality. It was dried (Na) and redistilled. The nitrobenzene (" AnalaR ") was likewise dried ($CaCl_2$) and redistilled. Solutions of the freshly distilled acid chloride in benzene, and of aluminium chloride in nitrobenzene, were prepared in graduated flasks and brought to the temperature of the thermostat. The concentration of nitrobenzene (by volume) was maintained throughout the experiments at 20 c.c. in 180 c.c. of reacting solution.

The required quantity of benzene was added from a burette to a three-necked reaction flask immersed in the thermostat. The flask was fitted with a mercury-seal stirrer, an inlet tube, and a double-surface condenser to which was attached a guard-tube containing calcium

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[4] Dawson, *J. Amer. Chem. Soc.*, 1928, **50**, 133.

chloride. The solution of aluminium chloride was then added, followed by that of the acid chloride. The gaseous products of the reaction were swept out by nitrogen (flowing at about 200 c.c./min.), the liquid being rapidly and continuously stirred in order to obtain a smooth trace on the recorder.

Calculation of Results.—The recorder furnished a curve showing variation of scale-reading against time. This was converted by means of the sensitivity calibration curve into a graph showing the percentage of liberated carbon monoxide at any time (*t*) and integration afforded a figure of the actual volumes of the gas evolved in a selected interval of time.

Absolute constancy in the flow of nitrogen was not attainable and the slight variations during each 30 min. period, the interval adopted for the calculation in the slower reactions, were averaged. The volume V c.c. of carbon monoxide evolved per minute was given by :

$$V = \frac{273}{T} \times \frac{P}{760} \times 60 \times F \times \frac{0{\cdot}05 \times 0{\cdot}3 \times N}{100}$$

where T is the absolute temperature of the mixed gases, P is their pressure (mm. Hg), F (c.c./sec.) is the rate of flow of nitrogen, and N the number of integration squares in the appropriate units; this volume was subject to a correction dependent on the purity (usually ~97·9%) of the carbon monoxide used in calibrating the gas analyser.

Results.—In Table 1 are given details of three experiments to illustrate consistency. The decrease in the first-order constant may be attributed partly to ketone formation as a result of reaction between the acid chloride and the product, *tert.*-butylbenzene (cf. Part VII [2]), and partly to the decrease in the efficiency of the catalyst owing to complex formation between it and the ketone. The first-order constant for the particular concentration of aluminium chloride was obtained by extrapolation of the individual constants back to zero time in the case where acid chloride was greatly in excess of aluminium chloride. In all other cases, the figure over the time indicated was calculated by the method of least squares (although usually the figures obtained by the two methods were nearly identical); in these cases there was not a continuous variation in the value of k_1 (cf. Table 2).

TABLE 1.

$AlCl_3$ = 0·063 mole/l. $CMe_3{\cdot}COCl$ = 0·326 mole/l. Temp., 20·36°.

	CO (mole/l.) (corr.)			10^2k_1 (min.$^{-1}$)		
Time (min.)	Expt. 1	2	3	Exp. 1	2	3
60	0·050	0·049	0·052	0·273	0·271	0·288
120	0·084	0·088	0·092	0·250	0·259	0·275
180	0·109	0·116	0·121	0·229	0·243	0·258
240	0·128	0·136	0·143	0·208	0·225	0·241
300	0·143	0·151	0·159	0·192	0·208	0·222
360	0·154	0·163	0·170	0·178	0·193	0·206
10^2k_1 (extrapolated)				0·295	0·292	0·308

More consistent figures for the first-order constant were obtained when the catalyst was in excess. Table 2 shows reasonably constant figures up to 85% of the reaction (120 min.).

TABLE 2.

$[AlCl_3]$ = 0·15 mole/l. $[CMe_3{\cdot}COCl]$ = 0·05 mole/l. Temp., 20·36°.

Experiment 31.

Time (min.)	30	60	90	120	150	180	210	240
CO (mole/l.) (corr.)	0·0198	0·0316	0·0385	0·0427	0·0451	0·0470	0·0481	0·0490
10^2k_1 (min.$^{-1}$)	1·68	1·67	1·63	1·60	1·55	1·56	1·52	1·63

10^2k_1 = 1·74 min.$^{-1}$ (extrap.), 1·65 min.$^{-1}$ (not extrap.; 60 min.).

A direct comparison with the titration method was carried out by arranging duplicate reactions in the same thermostat. In the titration method it is possible to calculate the first-order constant from the slope of the curve obtained by plotting log concentration against time, because, owing to compensatory influences, side-reactions have a smaller effect on the consumption of the acid chloride. The two determinations, in which the concentrations and temperature of Table 1 were used, afforded a mean value for 10^2k_1 of 0·299 min.$^{-1}$, negligibly different from that of 0·298 min.$^{-1}$ derived from the previous measurements. Slight differences in the first-order constants determined by the two methods barely reflect real differences since the rapid *initial* consumption of acid chloride is not paralleled by a very rapid rate of elimination of carbon monoxide. Although there is some uncertainty about the exact zero time, a comparison of acid chloride concentrations estimated by the two procedures (Table 3) shows a lag in the evolution of carbon monoxide which is apparently partly due to irreversible formation of a complex which has a finite time of decomposition, and partly due to side-reactions mentioned above.

TABLE 3. *Pivaloyl chloride remaining after time, t. Concns. and temp. as in Table* 1.

t (min.)	60	120	180	240	300	360
Titration method (%)	74·2	60·1	49·7	42·3	36·5	31·9
CO evolution method (%)	84·6	72·9	64·6	58·4	52·5	49·3
Difference (%)	10·4	12·8	14·9	16·1	16·0	17·4

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