

Gas-phase pyrolytic reactions. Rate data for the pyrolysis of phenyl-N-tert-butylcarbamate and the Hammett correlation for pyrolysis of N-tert-butylbenzamides

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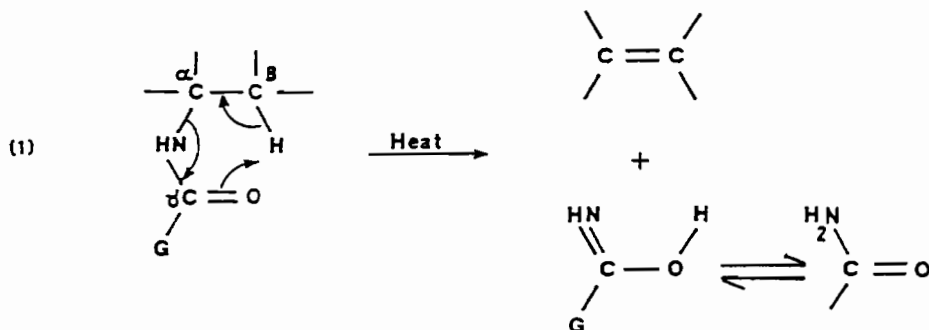
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ABSTRACT

Rates of gas-phase thermal elimination of phenyl-N-tert-butylcarbamate have been measured between 593 and 648 K and compared to that of N-tert-butylbenzamide and N-tert-butylacetamide. Also the gas-phase elimination reaction of substituted N-tert-butylbenzamides into alkene and substituted benzamides have been studied. The data give a good correlation with σ^0 value with $\rho + 0.43$ at 720 K.

INTRODUCTION

Amides with N-alkyl groups containing β -hydrogen atoms are able to eliminate alkenes as do esters, their oxygen analogues, and give the nitrogen analogues of carboxylic acids, namely primary amides. Since nitrogen is less electron-withdrawing than oxygen, polarization of the C-N bond, the principle driving force for the reaction Eqn. 1 is more difficult.



Consequently, the temperature of elimination is approximately 100° higher than that needed for esters (Taylor 1979). Bailey & Bird (1958) showed that, as in the case of esters, tertiary amides eliminate more readily than secondary amides and also N-phenylamide (G Ph) eliminate faster than the corresponding N-methylamide (G Me). In this paper, we have investigated the effect of a more electron-withdrawing

group (G OPh) on the elimination rate. The effect of different G groups Me, Ph and OPh on the elimination reaction rate of esters and amides has been discussed.

There have not been any studies on the Hammett correlations in the elimination reaction of amides, as it was believed to be difficult (Taylor 1975) due to accompanying side-reactions which are compounded by the higher temperature required. In our analytical flow apparatus, this side reaction is eliminated, because of the short residence time (30 s) needed for the substrate to pass through the reaction vessel. With the help of the nitrogen carrier gas, the unreacted substrate together with the decomposition product will flow to the gas chromatograph for analysis. As soon as the products are produced, they will be swept out of the reaction vessel and they will not be subjected to high temperature for secondary decomposition. Thus, this is the first study of the Hammett correlation in the gas-phase for isobutene elimination reaction of N-tert-butylbenzamides.

RESULTS AND DISCUSSION

The kinetic data for the pyrolysis of amides together with the temperature of measurements are given in Table 1 for PhOCONHCMe₃ and in Table 2 for ArCONHCMe₃.

Table 1. Kinetic data and Arrhenius parameters for the pyrolysis of PhOCONHCMe₃.

T/K	10 ³ k/s ⁻¹	log A/s ⁻¹	E _a /KJ mol ⁻¹
593.7	2.3	10.6 ± 0.5	151 ± 6.0
609.5	5.0		
623.7	8.9		
638.4	15.8		
648.0	30.9		

The compounds were each well behaved kinetically, and gave excellent first-order rate constants with linearity of 95% reaction and with no deviation in the Arrhenius plots. Each rate data coefficient represents an average of four kinetic runs, in agreement to within ±2% rate spread. The kinetic profile of each compound was scanned over a 50 K temperature range. The kinetic rate using an empty carbonized reaction vessel was compared with that for a similar vessel packed with glass helices. This increase in the surface to volume of approximate nine-fold does not affect the kinetic rate. The Arrhenius parameters seem to be in agreement with the pathways proposed for these reactions (Hurd & Blunk 1938). The kinetic consequences of changing G from Me to a Ph group and Ph to OPh group on the elimination reaction of amides and esters are recorded in Fig. 1. Comparison of the kinetic data reveals that the greater electron-withdrawing group, OPh, has increased the elimination reaction rate relative to Ph and Me groups by aiding C–N cleavage. Also Fig. 1 shows that this R group effect is greater in amides than in esters.

The value of log k_{rel} together with the rates of the pyrolysis of each compound at 720 K from the Arrhenius plot are given in Table 3. The data gave good correlation with σ^0 . Figure 2 shows a plot of the log k_{rel} values against σ^0 values which yield a ρ factor of 0.429 at 720 K. We have chosen 720 K as a temperature most nearly experimentally accessible to the amides under investigation. Applying the $\rho T = \rho' T'$

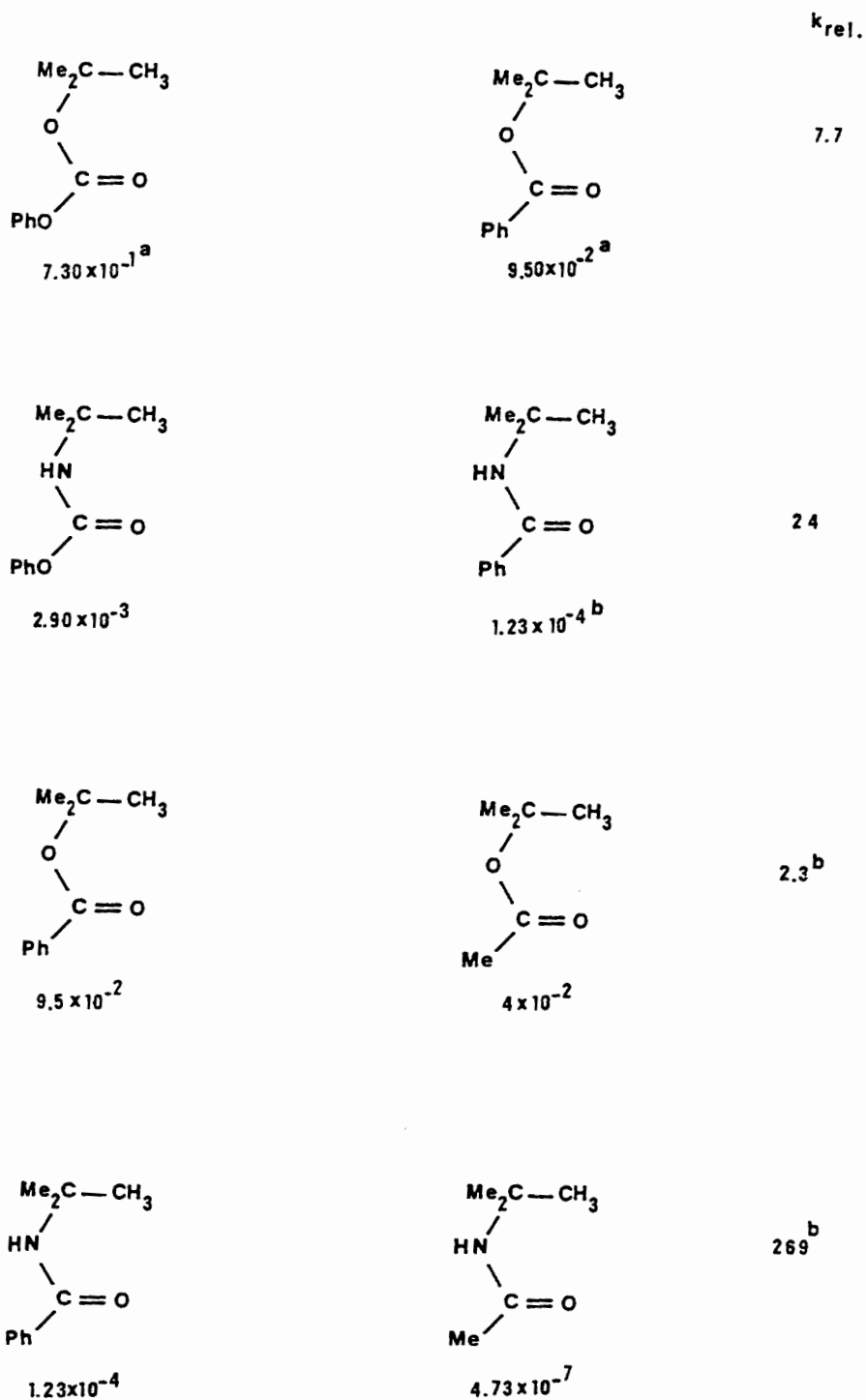


Fig. 1. Relative reactivities at 600 K for $[\text{PhOCOOCMe}_3]/[\text{PhCOOCMe}_3]$, $[\text{PhOCONHMe}_3]/[\text{PhCONHMe}_3]$, $[\text{PhCOOCMe}_3]/[\text{MeCOOCMe}_3]$ and $[\text{PhCONHMe}_3]/[\text{MeCONHMe}_3]$.

Table 2. Kinetic data and Arrhenius parameters for pyrolysis of X-C₆H₄CONHMe₃.

X	T/K	10 ³ k/s ⁻¹	log A/s ⁻¹	E _a /KJ mol ⁻¹
p-NO ₂	683.0	16.2	11.4 ± 0.1	172 ± 1.9
	693.0	25.1		
	702.8	38.0		
	712.9	57.5		
	722.7	85.1		
m-Cl	704.2	26.9	11.2 ± 0.0	172 ± 0.0
	714.3	40.7		
	724.6	60.3		
	735.3	89.1		
	746.3	132		
	751.9	191		
p-Cl	698.0	21.5	11.8 ± 0.1	181 ± 1.0
	708.5	34.0		
	718.3	51.4		
	728.1	76.9		
	738.3	116		
	748.0	169		
m-OMe	683.6	8.2	11.3 ± 0.5	175 ± 7.3
	690.5	9.9		
	702.9	19.9		
	710.5	27.9		
	720.7	43.2		
	727.9	58.4		
	731.0	66.4		
	748.2	126		
m-Me	705.0	17.4	12.3 ± 0.6	190 ± 7.9
	710.0	21.8		
	719.0	32.3		
	729.0	49.0		
	743.8	63.0		
	753.2	89.0		
p-OMe	705.0	18.1	12.9 ± 0.46	199 ± 6.4
	710.0	22.7		
	719.0	34.0		
	729.0	52.5		
	743.8	67.1		
	753.2	95.3		

Table 3. Pyrolysis of compounds X-C₆H₄CONHMe₃.

X	10 ³ k (720 K)	log K _{rel} (720 K)
p-NO ₂	79.2	0.32
m-Cl	50.0	0.12
p-Cl	48.9	0.11
m-OMe	40.0	0.03
H ^a	39.8	0.00
m-Me	35.5	-0.03
p-OMe	28.4	-0.12

^a Literature value (Al-Awadi 1990).

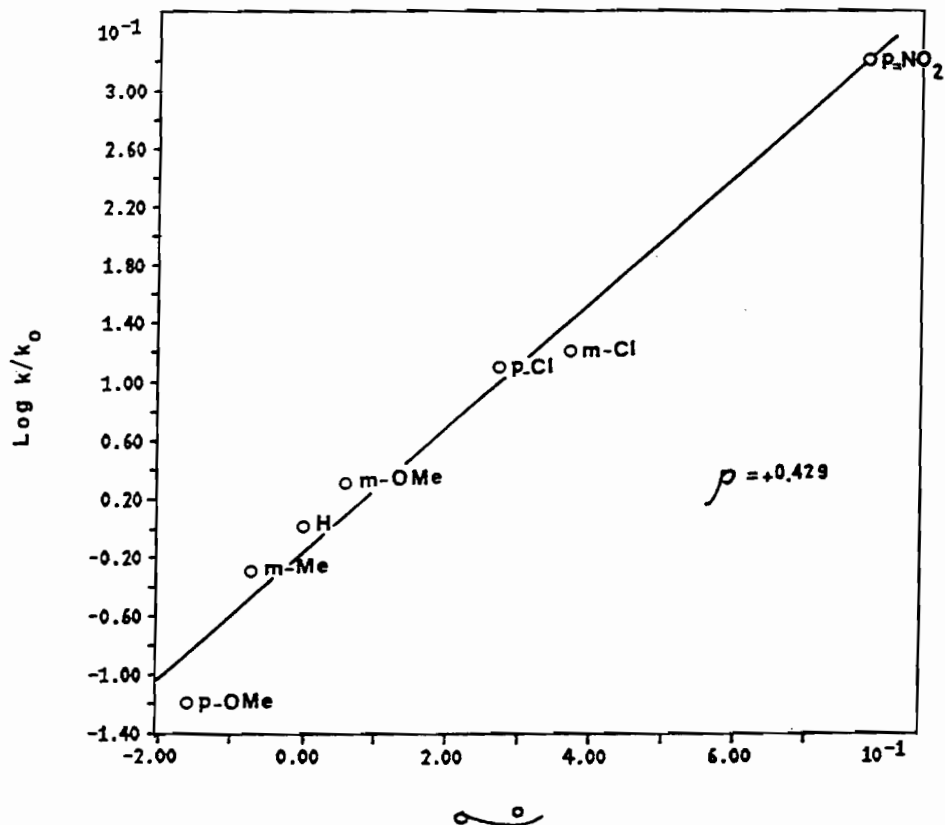


Fig. 2. Hammett correlation for pyrolysis of PhCONHMe_3 at 720 K.

relationship, we find that ρ -factor is 0.51 at 600 K. By comparing this value with that for the elimination reaction of tert-butylbenzoate which is 0.58 at 600 K (Amine and Taylor 1975), one would say that there is less negative charge developed at the γ -carbon in the transition state for pyrolysis of tert-butylbenzamide than for tert-butylbenzoate.

EXPERIMENTAL

Kinetic studies and product analysis:

The flow system used for measuring reaction rates consists of two main parts: A CDS custom made pyrolysis unit where the reaction takes place, coupled to a Varian 3300 gas chromatograph, where the products of the reaction and the residual reactants are analyzed. The pyrolysis unit consisted of an insulated aluminium block, a glass reactor vessel, a platinum resistance thermometer and a thermocouple connected to a Comark micro-processor thermometer. The internal surface of the reaction vessel was deactivated by injecting 4–5 portions of 50 μl of allyl bromide at 450°C in the absence of air. This process has coated the internal surface of the tube with a homogeneous carbon film (DePuy & King 1960). The residence time of the sample vapour in the

glass reactor was 40–43 sec. A 15% SE-30 packed column on chromosorb W., AW., mesh size 80–100 of 2 m length and 1/8 OD with flow rate of nitrogen carrier gas of 25–30 ml/min. was used in the analysis. The technique used for product analysis has been described by DePuy & King (1960) and Al-Awadi (1990).

Synthesis:

Ph-N-tert-butylcarbamate was prepared from the reaction of phenylchloroformate with tert-butylamine in the presence of pyridine in 77% yield, m.p. 98–99°C from petroleum ether 60–80°C; δ_{H} (CDCl₃) 7.5 (5H, m), 5.3 (1H, s), 1.5 (9H, s); (Found: C, 68.6; H, 7.6; N, 7.0; C₁₁H₁₅NO₂ requires C, 68.4; H, 7.8; N, 7.3%).

N-tert-butylbenzamides was prepared from the reaction of substituted benzoyl chloride with tert-butylamine. p-NO₂C₆H₄CONHCMe₃, 79%, m.p. 146–147°C from ethanol-water; δ_{H} (CDCl₃) 9.5 (1H, s); 8.25 (2H, d), 7.9 (2H, d), 1.5 (9H, s); (Found: C, 58.9; H, 6.0; N, 11.9; C₁₁H₁₄N₂O₃ requires C, 59.4; H, 6.3; N, 12.6%).

m-ClC₆H₄CONHCMe₃, 73%, m.p. 102°C from petroleum ether 60–80°C; δ_{H} (CDCl₃) 9.8 (1H, s), 7.65 (1H, s), 7.55 (1H, d), 7.4 (1H, d), 7.25 (1H, t), 1.5 (9H, s); (Found: C, 62.1, H, 6.5; N, 6.8; C₁₁H₁₄NOCl requires C, 62.4; H, 6.6; N, 6.9%).

p-ClC₆H₄CONHCMe₃, 75%, m.p. 132–133°C from petroleum ether 40–60°C; δ_{H} (CDCl₃) 9.8 (1H, s), 7.7 (2H, d), 7.4 (2H, d), 1.5 (9H, s); (Found: C, 62.1, H, 6.5; N, 6.9; C₁₁H₁₄NOCl requires C, 62.4; H, 6.6; N, 6.9%).

m-CH₃OC₆H₄CONHCMe₃, 70%, m.p. 106°C from petroleum ether 60–80°C; δ_{H} (CDCl₃) 9.9 (1H, s), 7.8 (1H, s), 7.7 (1H, d), 7.6 (1H, d), 3.8 (3H, s), 1.5 (9H, s); (Found: C, 69.3; H, 8.1; N, 7.3; C₁₂H₁₇N₂O requires C, 69.5; H, 8.2; N, 6.8%).

m-CH₃C₆H₄CONHCMe₃, 70%, m.p. 93°C from petroleum ether 40–60°C; δ_{H} (CDCl₃) 9.5 (1H, s), 7.5–7.6 (2H, m), 7.25 (2H, d), 2.3 (3H, s), 1.5 (9H, s); (Found: C, 75.4; H, 9.0; N, 7.7; C₁₂H₁₇NO requires C, 75.4; H, 8.9; N, 7.4%).

p-CH₃OC₆H₄CONHCMe₃, 69%, m.p. 116°C from petroleum ether 40–60°C; δ_{H} (CDCl₃) 9.8 (1H, s), 7.7 (2H, d), 6.85 (2H, d), 3.8 (3H, s), 1.5 (9H, s); (Found: C, 69.5; H, 8.3; N, 7.2; C₁₂H₁₇NO₂ requires C, 69.5; H, 8.2; N, 6.8%).

All compounds were indicated to be >99% pure by GLC analysis and gave the expected IR spectra.

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تفاعلات التحليل الحراري الغازية
معدلات تفاعل التحليل الحراري لمركبات فنيل ثلاثي بيوتيل الكارباميت وعلاقة هاميت
للتحليل الحراري لمركبات ثلاثي بيوتيل البنزاميد.

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خلاصة

لقد تم قياس معدلات لتفاعلات التحليل الحراري للفنيل ثلاثي بيوتيل الكارباميت بين درجات حرارة ٥٩٣ الى ٦٨٤ كالفن، وتم مقارنتها مع ثلاثي بيوتيل البنزاميد وثلاثي بيوتيل الاستاميد. كذلك تم دراسة تفاعلات الازاحة بالحالة الغازية لمشتقات ثلاثي بيوتيل البنزاميد والتي تتحلل الى الالكين ومشتقات البنزاميد. وقد اعطت هذه النتائج علاقة جيدة مع ثابت هذه المشتقات σ حيث انتجت ثابت التفاعل بقيمة $+0.34$ في درجة ٧٢٠ كالفن.

