936. *The Mechanism of the Reaction of Aryl* iso*Cyanates with Alcohols and Amines. Part VIII.*[1] *The Base-catalysed Reaction with Amines.*

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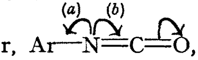
Kinetic examination of the reaction

$$\mathrm{Ar{\cdot}NCO + NH_2R \longrightarrow Ar{\cdot}NH{\cdot}CO{\cdot}NHR}$$

for various reactant pairs, in the presence of triethylamine and other tertiary amines (B) in dry benzene at 20° reveals that, superimposed upon the true spontaneous and product-catalysed reactions, are (1) a base-catalysed reaction,
$\mathrm{Ar{\cdot}NCO + B \rightleftharpoons Complex;\ Complex + NH_2R \longrightarrow Ar{\cdot}NH{\cdot}CO{\cdot}NHR + B}$,
and (2) a combined product–base–catalysed reaction involving mutual action by these two catalytic entities, possibly: $\mathrm{Ar{\cdot}NCO + B + Ar{\cdot}NH{\cdot}CO{\cdot}NHR \rightleftharpoons}$ ternary complex; ternary complex $\mathrm{+ NH_2R \longrightarrow 2Ar{\cdot}NH{\cdot}CO{\cdot}NHR +}$ B. With $\mathrm{B = NEt_3}$, the reaction velocity increases in the order $\mathrm{Ar = C_6H_{11}}$ (*cyclo*hexyl) $\ll$ *p*-$\mathrm{MeO{\cdot}C_6H_4}$ < Ph, *i.e.*, with increasing conjugation (*a*) of the nitrogen atom with Ar,  $\mathrm{Ar{-}N{=}C{=}O}$, which, competing with the conjugation (*b*), renders the carbonyl group more susceptible to nucleophilic attack. In agreement with this, for Ar = Ph, the catalytic effect is greater, the greater is the basic strength (nucleophilic power) of B, *i.e.*, $\mathrm{B = NEt_3}$ ($K_b = 5{\cdot}46 \times 10^{-4}$) > $\mathrm{C_5H_5N}$ ($K_b = 2{\cdot}3 \times 10^{-9}$), but, as in the alcohol reaction, the much weaker catalytic effect of $\mathrm{C_6H_5{\cdot}NMe_2}$ ($K_b = 1 \times 10^{-9}$) is anomalous, owing to sterically hindered attack.

Like the *iso*cyanate–alcohol reaction,[2a] the corresponding *iso*cyanate–amine reaction $\mathrm{Ar{\cdot}NCO + NH_2R \longrightarrow Ar{\cdot}NH{\cdot}CO{\cdot}NHR}$ is catalysed by tertiary amines.* The similar mechanisms already established for the spontaneous and base-catalysed alcohol reaction,[2] and for the spontaneous and product-catalysed amine reaction,[1] strongly suggest a mechanism ($\mathrm{B = NR_3}$):

$$\mathrm{Ar{\cdot}NCO + B \underset{k_8}{\overset{k_7}{\rightleftharpoons}} Complex;\ Complex + NH_2R \xrightarrow{k_9} Ar{\cdot}NH{\cdot}CO{\cdot}NHR + B} \quad . \quad \text{(i)}$$

as probable for the base-catalysed reaction with amines. Superimposition of such a base-catalysed reaction upon the spontaneous (k_s) and product-catalysed reactions (preceding paper) would require the experimental, second-order velocity coefficient k_e to be represented by the expression:

$$k_e = k_s + k_c'[\mathrm{Carb.}] + k_c[\mathrm{B}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where k_s and k_c' are functions of amine concentration.[1] Application of stationary state conditions gives the relation:

$$k_{bi} = k_c[\mathrm{B}] = k_e - (k_s + k_c'[\mathrm{Carb.}]) = k_7k_9[\mathrm{B}]/(k_8 + k_9[\mathrm{NH_2R}]) \quad . \quad \text{(iii)}$$

i.e., the linear relation,

$$1/k_c = [\mathrm{B}]/k_{bi} = k_8/k_7k_9 + [\mathrm{NH_2R}]/k_7 \quad . \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

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* To avoid confusion the term " base " (B) is used throughout for the tertiary-amine catalyst, and " amine " for the reactant amine $\mathrm{NH_2R}$. The various *k* values are denoted by subscripts which differentiate them from those used for the *k* values of concomitant reactions, described in Part VII.

[1] Part VII, preceding paper.

[2] Baker and Gaunt, *J.*, 1949, (*a*) 9, (*b*) 19, (*c*) 27.

where k_{bi} = the apparent second-order velocity coefficient for the isolated base-catalysed reaction.

The relations (iii) and (iv) can only be tested by the determination, at identical values of amine and urea concentration, of k_e in the presence of an added tertiary base, and of $k_s + k'$[Carb.] in the absence of the base. The second-order plots obtained in the presence of a base exhibit the same characteristics as those revealed in the spontaneous reaction (Part VII, Figure), the particular portions of this curve followed by the reaction depending on the initial concentration of the urea, on its solubility, and on the reaction rate.

System A * ($Ph{\cdot}NCO$-*p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$) was first examined with constant initial [Ph·NCO] (0·0726M) and [NH_2R] (0·1292M) in initially homogeneous media (*i.e.* initial [Carb. A] = 0) but with varying concentrations of triethylamine as the base catalyst, in dry benzene solution at 20°. The second-order plots of all such runs were shallow S-shaped curves in which k_e first increases as [Carb. A] increases until, after deposition of solid product, it then decreases. In all cases, however, the [Carb. A] builds up to 2—4 times its saturation value before crystallisation begins, *e.g.*:

[NEt_3] (10^{-3}M)	3·0	5·0	7·5	9·9	14·9	19·8	24·8	29·8
[Carb. A] at deposition (10^{-3}M)	20	18	28	14	24	26	27	28
Saturation [Carb. A] † (10^{-3}M) †	6·85	6·95	6·50	7·10	6·70	6·60	6·60	6·65

† At deposition: from data in Part VI (p. 4650).

The irregular nature of the commencement of product deposition from initially homogeneous media is again evident.

From these experiments (see p. 4668), plots (P1) of the instantaneous k_e values (as ordinates) against corresponding values of [Carb. A] (determined by either tangent or small interval methods) were made at different base concentrations, including the case when [NEt_3] = 0. These plots are all accurately linear, but the slope of the lines, *i.e.*, the apparent k_c' value, increases as [NEt_3] increases. From these graphs a second series of plots (P2) of k_e against [NEt_3] at constant [NH_2R] and constant [Carb. A] were made. The relevant data are in Table 1. These plots (P2) are again accurately linear, the slope of the lines increasing from No. 1 to 8, *i.e.*, the apparent k_c value increases as [Carb. A] increases and [NH_2R] decreases. This observed dependence of k_c on [Carb. A] or, alternatively, of k_c' on [NEt_3] is not accounted for by the mere superimposition of mechanism (i) alone (to give ii), and the inadequacy of this treatment is further revealed by the fact that the plot of $1/k_c$ against [NH_2R], although linear as required by equation

TABLE 1. *Values of* 10^5k_e *at constant* [NH_2R] *and* [*Carb. A*] *values for various values of* [NEt_3] *for system A.*

No.	1	2	3	4	5	6	7	8
[Carb. A] (10^{-2}M)	0	0·5	0·7	1·0	1·5	2·0	2·5	3·0
[NH_2R] (10^{-2}M) ...	12·92	12·42	12·22	11·92	11·42	10·92	10·42	9·92
[NEt_3] (10^{-2}M)	10^5k_e							
0	2·00	3·90	4·50	5·50	7·20	9·00	10·8	12·4
0·298	12·6	14·9	15·8	17·1	19·7	21·9	24·2	26·5
0·496	16·1	19·0	20·1	22·0	25·0	28·0	31·1	34·0
0·745	25·7	29·0	30·2	32·2	35·8	39·1	42·6	46·0
0·992	27·0	33·2	35·8	39·6	45·9	52·1	58·3	64·7
1·498	45·9	51·1	53·3	56·7	62·2	67·9	73·3	78·9
1·985	59·6	65·1	67·6	71·0	76·6	82·3	88·0	93·7
2·48	73·5	81·0	84·0	88·8	96·4	104	111	119
2·98	95·0	103	107	112	121	129	138	147

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* For key, see Part VII, preceding paper.

(iv), cuts the $1/k_c$ axis at a negative value when $[NH_2R] = 0$. This would require the impossible condition that k_8/k_7k_9 (equation iv) should have a negative value.

The increase in the apparent k_c' values with increase in $[NEt_3]$ means that the total effect of the urea and base catalysts, acting conjointly, is greater than the sum of their separate actions. This indicates a superimposed mechanism which involves both catalytic entities. Since previous evidence has suggested that the urea probably functions as an *acid* catalyst, the combined acid-catalysis by the product and base-catalysis by triethylamine could be envisaged as $Et_3N\rightarrow C(\because NAr)=O\rightarrow HN(Ar)\cdot CO\cdot NHR$, which is represented by

$$\mathrm{Ar{\cdot}NCO + Ar{\cdot}NH{\cdot}CO{\cdot}NHR + NEt_3} \underset{k_{11}}{\overset{k_{10}}{\rightleftharpoons}} \text{ternary complex *}$$

$$\text{ternary Complex} + \mathrm{NH_2R} \xrightarrow{k_{12}} \mathrm{2Ar{\cdot}NH{\cdot}CO{\cdot}NHR + NEt_3}$$

The new catalytic coefficient k_c'' would then be determined by the relation, $k_c''[\mathrm{ArNCO}][\mathrm{NEt_3}] = k_{10}k_{12}[\mathrm{Carb.\ A}][\mathrm{NEt_3}]/(k_{11} + k_{12}[\mathrm{NH_2R}])$. The experimental value of the composite second-order velocity coefficient k_e for the total base-catalysed reaction would then be represented by the sum:

$$k_e = k_s + k_c'[\mathrm{Carb.}] + k_c[\mathrm{B}] + k_c''[\mathrm{Carb.}][\mathrm{B}] \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

The data available permit an approximate test of this mechanism, since it requires that:

$$k_c''[\mathrm{Carb.}][\mathrm{B}] = k_e - (k_s + k_s'[\mathrm{Carb.}] + k_c[\mathrm{B}]) = K \quad . \quad . \quad . \quad \text{(vi)}$$

Hence, at constant [Carb.], $K/[\mathrm{B}]$ is a constant. This may be tested from the data available from plot P1. The values of k_e at [Carb.] = 0·020M were read off for various values of $[NEt_3]$; $k_s + k_c[\mathrm{B}]$ values are given by the intercepts on the k_e axis ([Carb. A] = 0); and k_c'[Carb.] from the plot when $[NEt_3] = 0$. The relevant results are in Table 2.

TABLE 2. *Values of $K/[B]$ for System A with triethylamine catalysis in dry benzene at 20° when [Carb. A] = 0·020M and $[NEt_3]$ is varied. (K in mole^{-1} l. sec.$^{-1}$.)*

$[NEt_3]$ (10^{-3}M)	2·98	4·96	7·45	9·92	14·98	19·85	24·8	29·8
10^5K	2·5	5·0	6·5	18	15	15·5	23·5	27·5
$10^5K/10^3[NEt_3]$	0·84	1·00	0·97	(1·80)	1·00	0·78	0·95	0·92

If the value in parentheses is neglected, the values of $K/[NEt_3]$ show a random variation around a constant value 0·92 ± 0·07, as required by (vi). In view of the approximations essential to this complicated analysis the agreement with the requirements of the composite mechanism (v) is regarded as satisfactory. It follows from this that the true base-catalytic coefficient k_c can be determined only at [Carb. A] = 0, *i.e.*, from the slope of the linear plot No. 1 of P2 (Table 1), in which k_e is plotted against $[NEt_3]$ at constant $[NH_2{\cdot}C_6H_4{\cdot}CO_2Et]$ and [Carb. A] = 0.

The validity of mechanism (i) and its derived relation (iv) for the isolated base-catalysed reaction was tested (for System A) by examination of the effect of variation in the initial $[NH_2R]$ from 0·0646 to 0·3877M when the initial concentrations of phenyl *iso*cyanate (0·0710M) and triethylamine (0·0121M) were maintained constant, in homogeneous media (initially [Carb. A] = 0). From the second-order plots, the varying values of k_e at increasing concentrations of [Carb. A] were determined as the reaction progressed. Plots (P3) of k_e against [Carb. A] are accurately linear, and from these the values of k_e at

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* The formation of such a ternary complex might, of course, involve successive equilibria between the *iso*cyanate and one catalytic entity to give a 1 : 1 complex, and between this 1 : 1 complex and the second catalytic entity to give a 1 : 2 complex.

[Carb. A] = 0 were determined. The relevant data are in Table 3, the values of k_c and its reciprocal thus obtained being independent of any interaction which occurs between triethylamine and product catalysis. With increasing [$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$], k_o increases, but both k_e and k_{bi} decrease as required by equation (iii), and the plot of $1/k_c$ against [$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$] is linear, thus satisfying the derived relation (iv). Thus the values $k_7 = 0{\cdot}089$ and $k_9/k_8 = 0{\cdot}04$ are derived.

TABLE 3. *Variation of k_c with* [NH_2R] *in dry benzene at* 20° ($R = C_6H_4{\cdot}CO_2Et$)

Initially: [Ph·NCO] = 0·0710M; [Carb. A] = 0; [NEt_3] = 0·0121M.

No.	Initial [NH_2R] (10^{-2}M)	10^5k_o *	10^5k_e	$10^5k_{bi} = 10^5k_c$ [NEt_3]	10^2k_c	$1/k_c$
85	6·46	1·2	43·0	41·8	3·45	28·9
86	12·92	1·5	41·5	40·0	3·30	30·2
87	25·85	1·9	40·9	39·0	3·22	31·0
88	31·02	2·1	40·2	38·1	3·14	31·7
89	38·77	2·5	39·7	37·2	3·07	32·5

* $k_o = k_s + k_c'$ [Carb.]; since [Carb. A] = 0, $k_o = k_s$.

In heterogeneous media, *i.e.*, those initially saturated with Carb. A, supersaturation phenomena make reproducibility of conditions more difficult, and the steady values of k_e (*i.e.*, those when the second-order plots have become linear), although showing a general trend towards decreasing as the initial [$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$] increases, are somewhat erratic, as shown in Table 4. In order to smooth out these experimental errors the smoothed plots of k_e and k_o against initial [$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$] were subtracted to give the plot of $k_{bi}(= k_e - k_o)$ against [$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$]. The derived values are given in Table 5.

TABLE 4. *Variation of k_e with varying initial* [NH_2R] *for the base-catalysed system A in heterogeneous media initially saturated with Carb. A* ($R = C_6H_4{\cdot}CO_2Et$).

Initially: [Ph·NCO] = 0·0708M; [NEt_3] = 0·0120M throughout.

No.:	90	91	92	93	94	95	96
Initial [NH_2R] (10^{-2}M)	46·61	38·83	31·10	25·92	12·96	6·48	3·24
Saturation [Carb. A] (10^{-2}M)	2·46	2·07	1·70	1·44	0·80	0·48	0·32
10^5k_e	44·8	46·2	44·2	48·2	46·1	49·6	56·1

TABLE 5. *Smoothed values of k_c at various* [NH_2R] *in System A in heterogeneous media* ($R = C_6H_4{\cdot}CO_2Et$).

[NH_2R] (10^{-2}M)	10^5k_e	10^5k_o	10^5k_{bi}	10^2k_c	$1/k_c$	[NH_2R] (10^{-2}M)	10^5k_e	10^5k_o	10^5k_{bi}	10^2k_c	$1/k_c$
5	52·0	4·7	47·3	4·63	21·5	30	46·2	9·3	36·9	3·61	27·6
10	48·7	5·5	43·2	4·23	23·6	40	44·9	11·1	33·8	3·31	30·1
20	47·5	7·5	40·0	3·92	25·5	50	43·6	13·0	30·6	3·00	33·3
25	46·8	8·4	38·4	3·76	26·5						

Despite the fact that, in these systems, k''[Carb. A][B] is not zero, behaviour parallel to that shown in homogeneous media is observed, *i.e.*, (*a*) k_{bi} decreases as [NH_2R] increases as required by equation (iii), and (*b*) the plot of $1/k_c$ against [NH_2R] is linear (equation iv) as is required by mechanism (i). These results thus confirm the conclusions reached in the study in homogeneous media.

System C.—Owing to the greater speed of this reaction and the greater insolubility of the product, this system cannot be examined under homogeneous conditions, but a more limited series of experiments in media saturated with Carb. C revealed the same general pattern, the initial high value of k_e decreasing to a value which then remained constant over a large percentage of the total reaction. The essential data are summarised in Table 6.

Effect of Varying the iso*Cyanate Component.*—Limited examination of systems B and D was made, chiefly in order to determine the effect of varying the nature of the *iso*cyanate on the velocity of the triethylamine-catalysed reaction with aniline. In system B, k_e

initially increases and then decreases to a constant value, whilst in system D the initial high rates rapidly decrease to give a k_e value which remains constant over ~30—80% of the reaction course.

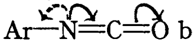
In triethylamine-catalysed systems of initial concentrations [Ar·NCO] = [NH_2Ph] = 0·07M, all saturated with respect of the products, the corresponding values of k_e and k_c are in Table 7. Thus, in base-catalysed systems, both k_e and the apparent k_c increase in the order Ar = $C_6H_{11} \ll$ *p*-MeO·C_6H_4 < Ph. This is in agreement with the postulated nucleophilic attack of amine and catalyst base on the polarised carbonyl group of the *iso*cyanate, the competing conjugation of the nitrogen with the carbonyl group  being at a maximum when all conjugation with the group Ar is eliminated in the *cyclo*hexyl compound, and the order is identical with that previously established[3] for the alcohol reaction.

TABLE 6. *Triethylamine-catalysed reaction of system C initially saturated with Carb. C, in dry benzene at* 20°.

Initially: [Ph·NCO] = [NH_2Ph] = 0·0698M.

No.	[NEt_3] (10^{-3}M)	Initial 10^5k_e	Mean steady 10^5k_e	Percentage reaction †
72	0	78·5	55·1 ± 0·6 (3) *	31·9—50·7
73	0·741	128	82·0 ± 1·5 (7)	22·6—63·5
74	1·48	127	113 ± 3 (8)	24·2—75·8
75	2·37	177	153 ± 5 (6)	47·2—77·8
76	2·97	211	183 ± 6 (6)	34·7—81·5
77	4·15	274	245 ± 4 (6)	40·8—85·4
78	5·94	369	331 ± 7 (5)	31·7—81·4

* Number of separate observations in parentheses.
† Over which a steady k_e value was observed.

TABLE 7. *Values of* k_e *and* k_c *for the triethylamine-catalysed systems* Ar·NCO–NH_2Ph.

	[NEt_3] (10^{-3}M)	0	3	6		[NEt_3] (10^{-3}M)	0	3	6
Steady 10^5k_e	Ar = Ph	58·4	169	314	10^3k_c	Ar = Ph	—	372	430
	Ar = *p*-MeO·C_6H_4	69·2	125	194		Ar = *p*-MeO·C_6H_4	—	192	212
	Ar = C_6H_{11}	1·04	1·11	1·20		Ar = C_6H_{11}	—	0·227	0·270

Variation of the Tertiary Base Catalyst.—System C was also examined with pyridine and dimethylaniline severally as the base catalysts. The results are summarised in Table 8, and should be compared with those for triethylamine in Table 7.

TABLE 8. *Values of steady* k_e *in System C catalysed by* NR_3 = (a) *pyridine, and* (b) *dimethylaniline in dry benzene at* 20°.

Initially: [Ph·NCO] = [NH_2Ph] = 0·070M.

No.	[NR_3] (10^{-3}M)	10^5k_e	10^3k_c	No.	[NR_3] (10^{-3}M)	10^5k_e	10^3k_c
—	0	58·4	—	(*b*) 105	5·919	58·8	10·4
(*a*) 102	3·061	82·3	77·8	106	11·84	70·9	
103	6·116	109		107	23·65	76·3	
104	12·24	149					

The stronger base triethylamine ($K_b = 5{\cdot}65 \times 10^{-4}$) is a much more effective catalyst than is the weaker pyridine ($K_b = 2{\cdot}3 \times 10^{-9}$), and the anomalous, very weak catalytic effect of the almost equally strong base dimethylaniline ($K_b = 1 \times 10^{-9}$), observed in the alcohol reaction and attributed to sterically hindered attack,[3, 2b] is again marked, although, in the amine reaction, a weak catalytic effect is detectable at high concentrations of this catalyst.

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[3] Baker and Holdsworth, *J.*, 1947, 713.

The composite mechanism (v) is the only one which satisfactorily accounts for the *iso*cyanate–amine reaction in the presence of a tertiary base catalyst. Each of the separate routes to the formation of the urea, however, reveals the same characteristic pattern previously established for the alcohol reaction, and is of the general form involving attack by an amine or alcohol molecule on a reversibly formed 1 : 1 or 1 : 2 complex between the *iso*cyanate and a catalytic entity, which may be the reactant amine or alcohol itself, the product, or an added tertiary base. There is thus a unified pattern throughout the whole of the reactions of aryl *iso*cyanates with nucleophilic reagents, but kinetic analysis is unable to provide information as to why the attack of a second molecule of the reactant seems to be essential to complete the proton-transfer to give the final product when the reactant itself is the catalyst.

EXPERIMENTAL

The preparation and purification of the materials used, and the experimental techniques were identical with those described in Part VII and in previous papers in this series. The tertiary bases were dried by long contact with potassium hydroxide. After careful fractionation, the fraction of constant boiling point was refluxed over freshly ignited calcium oxide, and again fractionated through an efficient column, giving: triethylamine, b. p. 89°; pyridine, b. p. 113°/752 mm.; dimethylaniline, b. p. 76°/15 mm. They were stored over potassium hydroxide and redistilled immediately before use.

The number of experiments is too large to permit individual record; analyses of the results are recorded in the various Tables. As an illustration, the experimental data for the system phenyl *iso*cyanate–benzocaine (system A) with triethylamine catalysis in dry benzene at 20°, from which the plots P1 (p. 4664) were obtained, are recorded.

Values of instantaneous k_e from the experimental second-order plots in a homogeneous system initially 0·0726M *in* Ph·NCO *and* 0·1292M *in benzocaine, for varying concentrations of triethylamine, up to the point* (*) *when deposition of product commenced. Concentrations are in mole l.*$^{-1}$.

No.	[NEt$_3$]	10^2[Carb. A]	10^2[NH$_2$·C$_6$H$_4$·CO$_2$Et]	10^5k_e
64	0·003	0·63	12·29	15·3
	,,	1·30	11·62	18·3
	,,	2·01 *	10·91	20·6
	,,	—	10·32	20·6
65	0·005	0·58	12·34	19·6
	,,	1·21	11·71	23·3
	,,	1·76 *	11·16	25·8
	,,	—	10·49	27·0
66	0·0075	0·63	12·29	30·6
	,,	1·23	11·69	33·5
	,,	1·76	11·16	35·6
	,,	2·27	10·65	41·1
	,,	2·81 *	10·11	44·8
	,,	—	9·65	46·8
67	0·010	0·33	12·59	30·5
	,,	0·84	12·08	37·9
	,,	1·38 *	11·54	44·0
	,,	—	11·03	46·6
68	0·015	0·50	12·42	49·2
	,,	0·96	11·96	57·8
	,,	1·51	11·41	63·7
	,,	2·01	10·91	66·1
	,,	2·43 *	10·49	73·5
		—	9·65	58·4
69	0·0199	0·92	12·00	69·7
	,,	1·26	11·66	74·0
	,,	1·89	11·03	78·0
	,,	2·26	10·66	84·0
	,,	2·64 *	10·28	90·1
70	0·0248	0·46	12·46	80·0
	,,	0·79	12·13	84·9
	,,	1·17	11·75	95·5
	,,	1·68	11·24	99·5
	,,	2·22	10·70	106
	,,	— *	9·77	90·3
71	0·0298	0·58	12·34	105
	,,	1·05	11·87	111
	,,	1·55	11·37	122
	,,	2·01	10·91	130
	,,	2·43	10·49	135
	,,	— *	9·69	115

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