

## Ion-pair Formation Studies : Part VI—Effect of Ion-pairs on Kinetics of Reaction Between Sodium Iodoacetate & Sodium Thiosulphate

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The kinetics of reaction between sodium iodoacetate and sodium thiosulphate has been studied at different ionic strengths and 296.16 K. The association constants of the ion-pair, NaIOAc have been calculated using Fuoss-Hsia equation with Fernandez-Prini coefficients from the conductance data and found to be 3.66 and 9.04  $\text{dm}^3 \text{mol}^{-1}$  at 296.16 and 308.16 K respectively. The rate constants at zero ionic strength for the reaction due to free ions and ion-pairs have been separated from the observed rate constants at different ionic strengths and found to be 0.334 and 9.93  $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$  respectively at 296.16 K. The extent of participation of ion-pairs in the reaction increased with ionic strength of the solution and found to be 12.1% over the ionic strength range (0.004–0.025) studied.

S RIVASTAVA<sup>1</sup> reported the kinetics of reaction between sodium iodoacetate and sodium thiosulphate in different aquo-organic solvents at 20°. However, this data was not analysed to find the extent of participation of ion pairs in the above reaction. The association constants of sodium iodoacetate in water were also not reported earlier. In our previous communication<sup>2</sup> we have studied the effect of ion-pairs on the kinetics of reaction between potassium peroxydisulphate and potassium iodide and showed that iodide ion is oxidized not only by  $\text{S}_2\text{O}_8^{2-}$  but also by the ion pair  $\text{KS}_2\text{O}_8^-$  simultaneously. In continuation of this work we have carried out a detailed investigation of the kinetics of iodoacetate-thiosulphate reaction at different ionic strengths to find out whether ion-pairs participate in this reaction and if so to what extent. Also the conductances of the solutions of sodium iodoacetate in water were measured to find the association constants required for the analysis of the kinetic data.

### Materials and Methods

Sodium iodoacetate (Fluka) was used after repeated crystallizations from ethanol and dried *in vacuo* over  $\text{P}_2\text{O}_5$ . Sodium thiosulphate was of BDH (AR) grade and used as such. The water used was triply distilled and had a specific conductance less than  $5 \times 10^{-7} \text{Scm}^{-1}$ . Equimolar concentrations of sodium iodoacetate and sodium thiosulphate were taken for each kinetic set and the ionic strength varied by varying the concentrations of the reactants themselves. The reaction was followed at 296.16K by estimating the unreacted thiosulphate with standardized iodine solution using starch as indicator. The experimental details of measuring the conductance was the same as reported earlier<sup>3</sup>. All the conductance values were corrected for solvent conductance. The overall accuracy of the measured conductance was within  $\pm 0.05\%$ .

### Results

The observed molar conductances of sodium iodoacetate in water at 296.16 K and 308.16 K presented in Table 1. The dielectric constants and viscosities were taken from literature<sup>4a</sup>.

The conductance data was first analysed using Shedlovsky extrapolation technique<sup>5</sup> according to which

$$1/\Delta S(Z) = 1/\Delta_0 + (K_A/\Delta_0^2) c\Delta y_{\pm}^2 S(Z) \dots (1)$$

where  $K_A$  is the association constant and other symbols have their usual significance. The activity coefficient  $y_{\pm}$  was calculated using the Debye-Huckel limiting law equation<sup>4b</sup>

$$\log y_{\pm} = -A(\alpha c)^{1/2} \dots (2)$$

TABLE 1— MOLAR CONDUCTANCE OF SODIUM IODOACETATE IN WATER AT 298.16 and 306.16 K.

| $c \times 10^4 / \text{mol dm}^{-3}$ | $\Lambda / \text{Scm mol}^{-1}$ |         |
|--------------------------------------|---------------------------------|---------|
|                                      | 296.16K                         | 306.16K |
| 50.149                               | 82.250                          | 99.467  |
| 37.612                               | 83.091                          | 100.91  |
| 30.089                               | 83.749                          | 101.94  |
| 25.075                               | 84.173                          | 102.66  |
| 21.492                               | 84.526                          | 103.27  |
| 18.806                               | 84.807                          | 103.64  |
| 16.716                               | 85.016                          | 104.16  |
| 15.045                               | 85.243                          | 104.35  |
| 12.537                               | 85.527                          | 104.83  |
| 10.030                               | 85.946                          | 105.46  |
| 8.3582                               | 86.226                          | 106.00  |
| 7.1642                               | 86.432                          | 106.33  |
| 6.2686                               | 86.491                          | 106.62  |
| 5.0149                               | 86.877                          | 107.05  |

$D = 78.303$  and  $\eta = 0.008903$  poise at 296.16 K; and 74.83 and 0.07194 poise at 306.16 K respectively.

where  $A = 1.8246 \times 10^6 / (DT)^{3/2}$  ( $D$  is the dielectric constant of the solvent at absolute temperature  $T$ ). The degree of dissociation,  $\alpha$  is related to  $S(Z)$  by Eq. (3).

$$\alpha = \Lambda S(Z) / \Lambda_0 \quad \dots (3)$$

Starting from an approximate initial value of  $\Lambda_0$ , the values  $Z$ ,  $S(Z)$ ,  $\alpha$  and  $y_{\pm}$  were calculated with the help of a computer in order to find the least square regression values of the slope ( $K_A / \Lambda_0^2$ ) and intercept ( $1 / \Lambda_0$ ) according to Eq. 1. The slope and intercept values were then used to evaluate  $\Lambda_0$  and  $K_A$ . The above procedure was repeated using the fresh value of  $\Lambda_0$  until the difference in the successive values was within  $\pm 0.005\%$ . Usually the convergence was obtained within three cycles. These final values of  $\Lambda_0$  and  $K_A$  were used as the initial values in further and more accurate analysis of the conductance data as described below.

The conductance data was then analysed using the Fuoss-Hsia equation<sup>6</sup> with Fernandez-Prini coefficients<sup>7</sup>. This equation is written as

$$\Lambda = \Lambda_0 - S(\alpha c)^{1/2} + E \alpha \ln(\alpha c) + J_1 \alpha c - J_2 (\alpha c)^{3/2} - K_A \Lambda y_{\pm}^2 \alpha c \quad \dots (4)$$

where the various symbols have their usual significance. The activity coefficients ( $y_{\pm}$ ) were calculated from the equation<sup>4c</sup>

$$-\log y_{\pm} = A (\alpha c)^{1/2} / \{1 + Ba (\alpha c)^{1/2}\} \quad \dots (5)$$

Starting with the initial values of  $\Lambda_0$  and  $K_A$  obtained from Shedlovsky method and equating the ion-size parameter ( $a$ ) to the Bjerrum critical distance ( $q$ ) the improved values of  $\Lambda_0$  and  $K_A$  were calculated using the least square fitting procedure<sup>8,9</sup>. The standard deviation ( $\sigma$ ) was calculated from the relation

$$\sigma = \{\sum (\Lambda_{\text{expl}} - \Lambda_{\text{calc}})^2 / (N-3)\}^{1/2} \quad \dots (6)$$

where  $N$  is the number of experimental points. These calculations were carried out on a TDC-12 computer and the results are summarized in Table 2.

### Discussion

From the study of the reaction between IOAc<sup>-</sup> and  $S_2O_3^{2-}$  Srivastava<sup>1</sup> concluded that it is a second order reaction being first order with respect to each reactant and an  $S_N^2$  mechanism has been suggested.

TABLE 2 — ASSOCIATION PARAMETERS OF SODIUM IODOACETATE IN WATER USING THE FUOSS-HSIA EQUATION

| T/K    | $q(A^\circ)$ | $\Lambda_0$<br>(S cm <sup>2</sup> mol <sup>-1</sup> ) | $K_A$<br>(dm <sup>3</sup> mol <sup>-1</sup> ) | $\sigma$ | $\Lambda^\circ \text{IOAc}^-$<br>(S cm <sup>2</sup> mol <sup>-1</sup> ) |
|--------|--------------|---|---|----------|---|
| 298.16 | 3.578        | 88.703<br>(88.669)                                    | 3.662<br>(2.990)                              | 0.053    | 38.60   |
| 308.16 | 3.613        | 109.52<br>(109.44)                                    | 9.045<br>(7.850)                              | 0.131    | 47.98   |

Values obtained from Shedlovsky method are given in parenthesis.

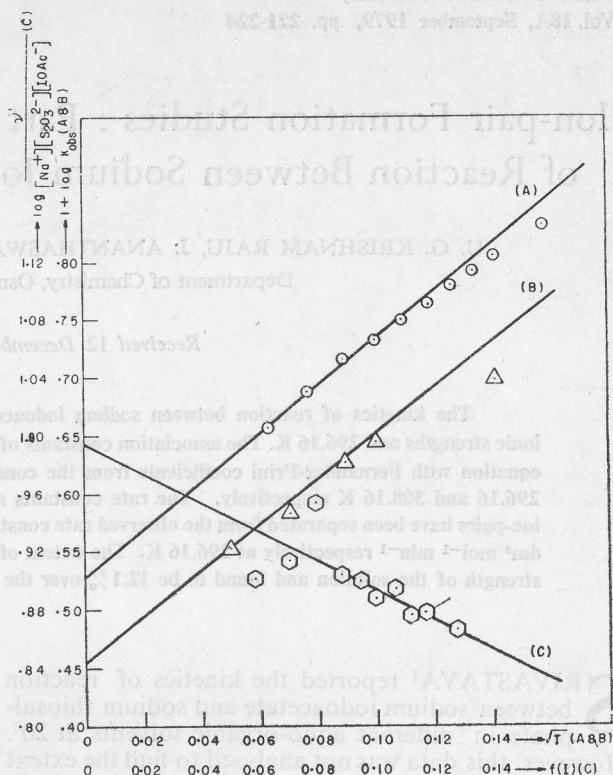
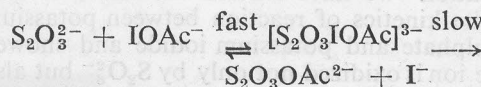


Fig. 1 — Plot of  $\log k_{\text{obs}}$  versus  $I^{1/2}$  (curves A and B at low and high ionic strengths respectively) and the plot of  $v / \{\log [\text{Na}^+] i\text{S}_2\text{O}_3^{2-} [\text{IOAc}^-]\}$  versus  $f(I)$  (curve C)



The rate law was also given as

$$-d[\text{S}_2\text{O}_3^{2-}] / dt = k_{\text{obs}} [\text{IOAc}^-]_{\text{total}} [\text{S}_2\text{O}_3^{2-}]_{\text{total}} \quad \dots (7)$$

According to Brønsted-Bjerrum equation<sup>10</sup> for aqueous systems at 25°

$$\log k = \log k_0 + 1.018 Z_A Z_B I^{1/2} \quad \dots (8)$$

Here  $Z_A$  and  $Z_B$  are the charges of the reactants. The slope of the plot of  $\log k_{\text{obs}}$  vs  $I^{1/2}$  should be 2.036 for the above reaction. In the present work at low ionic strengths, i.e. upto  $I = 0.01$  the slope was found to be 2.04 (Fig. 1A) in accordance with the theoretical value. However, as the ionic strength increased the experimental points deviated from the theoretical line (Fig. 1B). This could be due to the participation of ion-pairs. Hence the rate law for the reaction may be written as

$$-d[\text{S}_2\text{O}_3^{2-}] / dt = k_1^0 [\text{IOAc}^-] [\text{S}_2\text{O}_3^{2-}] y_1 y_2 / y_3 + k_2^0 [\text{IOAc}^-] [\text{NaS}_2\text{O}_3^-] y_1^2 / y_2 + k_3^0 [\text{NaIOAc}] [\text{S}_2\text{O}_3^{2-}] + k_4^0 [\text{NaIOAc}] [\text{NaS}_2\text{O}_3^-] \quad \dots (9)$$

where  $y_1$ ,  $y_2$  and  $y_3$  are the activity coefficients of the uni-, bi-, and trivalent species present in the solution. The fourth term in Eq. 9 was neglected as the concentrations of the ion-pairs are low (association constants being small) and the product  $[\text{NaIOAc}] [\text{NaS}_2\text{O}_3^-]$



$O_3^-]$  would be very small. By incorporating the association constants

$$K_1 = [\text{NaIOAc}] / [\text{Na}^+] [\text{IOAc}^-] y_1^2 \quad \dots (10)$$

$$K_2 = [\text{NaS}_2\text{O}_3^-] / [\text{Na}^+] [\text{S}_2\text{O}_3^{2-}] y_2 \quad \dots (11)$$

Eq. (9) can be rewritten as

$$-d[\text{S}_2\text{O}_3^{2-}] / dt = [\text{IOAc}^-] [\text{S}_2\text{O}_3^{2-}] \{k_1^0 y_1 y_2 / y_3 + [k_{ip}^0 / [\text{Na}^+] y_1^2 (K_2 k_2^0 + K_1 k_3^0)]\} \quad \dots (12)$$

or

$$-d[\text{S}_2\text{O}_3^{2-}] / dt = k_1^0 [\text{IOAc}^-] [\text{S}_2\text{O}_3^{2-}] y_1 y_2 / y_3 + k_{ip}^0 [\text{Na}^+] [\text{IOAc}^-] [\text{S}_2\text{O}_3^{2-}] y_1^2 \quad \dots (13)$$

where  $k_1^0$  is the rate constant for free ions and  $k_{ip}^0$  that of ion-pairs at zero ionic strength. The first term of Eq. (13) refers to the simple reaction between  $\text{IOAc}^-$  and  $\text{S}_2\text{O}_3^{2-}$  ions and second term to the reactions due to ion-pair ( $k_{ip}^0 = {}_2K_2^0 + K_1 K_3^0$ ). Since the  $[\text{IOAc}]_{\text{total}}$  and  $[\text{S}_2\text{O}_3^{2-}]_{\text{total}}$  are equal to  $(1 + [\text{Na}^+] K_1 y_1^2) [\text{IOAc}^-]$  and  $(1 + [\text{Na}^+] K_2 y_2) [\text{S}_2\text{O}_3^{2-}]$  respectively. Eq. (7) can be written as

$$-d[\text{S}_2\text{O}_3^{2-}] / dt = k_{\text{obs}} (1 + [\text{Na}^+] K_1 y_1^2) (1 + [\text{Na}^+] K_2 y_2) [\text{IOAc}^-] [\text{S}_2\text{O}_3^{2-}] \quad \dots (14)$$

Equating (13) and (14) and rearranging we get

$$k_{\text{obs}} (1 + [\text{Na}^+] K_1 y_1^2) (1 + [\text{Na}^+] K_2 y_2) y_3 / y_1 y_2 = k_1^0 + k_{ip}^0 [\text{Na}^+] y_1 y_3 / y_2 \quad \dots (15)$$

The concentrations of free ions  $\text{Na}^+$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{IOAc}^-$  and activity coefficients  $y_1$ ,  $y_2$  and  $y_3$  were calculated as follows.

If  $m$  is the molar concentration of the reactants,  $\alpha$  and  $\beta$  are the degree of dissociation of the ion-pair  $\text{NaIOAc}$  and  $\text{NaS}_2\text{O}_3^-$  respectively, then the concentrations of  $\text{Na}^+$ ,  $\text{IOAc}^-$ ,  $\text{NaIOAc}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{NaS}_2\text{O}_3^-$  are  $(1 + \alpha + \beta) m$ ,  $\alpha m$ ,  $(1 - \alpha) m$ ,  $\beta m$  and  $(1 - \beta) m$  respectively. The ionic strength of the system and the thermodynamic association constants  $K_1$  and  $K_2$  are given by Eqs (16-18)

$$I = (1 + \alpha + 2\beta) m \quad \dots (16)$$

$$k_1 = (1 - \alpha) / (1 + \alpha + \beta) \alpha m y_1^2 \quad \dots (17)$$

$$k_2 = (1 - \beta) / (1 + \alpha + \beta) \beta m y_2 \quad \dots (18)$$

Activity coefficients were calculated using Davies, equation<sup>11</sup>

$$-\log y_i = AZ_i^2 \{ I^{1/2} / (1 + I^{1/2}) - 0.3 I \} = AZ_i^2 f(I) \quad (19)$$

To start with  $\alpha$  and  $\beta$  were assumed to be unity and the corresponding value of  $I$  was calculated from (16). This  $I$  was then substituted in Eq. (19) to get the values of  $y_1$ ,  $y_2$  and  $y_3$ . The value of  $\beta$  was assumed to be unity in Eq. (17) and taking  $K_1$  as 3.662  $\text{dm}^3 \text{mol}^{-1}$  (obtained from conductance measurements in the present work, Table 2) the value of  $\alpha$  was calculated. This  $\alpha$  was then substituted in Eq. (18) to get an improved value of  $\beta$ . For this the value of  $K_2$  was taken as 3.846  $\text{dm}^3 \text{mol}^{-1}$  from the work of Monk and Gimblett<sup>12</sup>. These  $\alpha$  and  $\beta$  values were then substituted in Eq. (16) to get an improved value of  $I$ . This procedure was repeated several times till constant values for  $\alpha$ ,  $\beta$  and  $I$  were obtained.

The values of  $I$ ,  $k_{\text{obs}}$ ,  $f(I)$  and  $\text{Na}^+$  are given in Table 3. According to Eq. (15) the plot of  $k_{\text{obs}} (1 + [\text{Na}^+] K_1 y_1^2) (1 + [\text{Na}^+] K_2 y_2) y_3 / y_1 y_2$  versus  $[\text{Na}^+] y_1 y_3 / y_2$  should be linear with an intercept  $k_1^0$  and slope  $k_{ip}^0$ . Such a linear plot was obtained (Fig 2A) in the present work and from the intercept and slope values  $k_1^0$  and  $k_{ip}^0$  were found to be 0.334 and 9.93  $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$  respectively. We have also analysed some of the kinetic data obtained by Srivastava and the results are tabulated in Table 3. The required value of  $K_1$  at 20° for the analysis of this data was extrapolated from the association constant data reported in the present work and  $K_2$  at 20° was obtained from the data of Monk and Gimblett<sup>12</sup>. The  $k_1^0$  and  $K_{ip}^0$  were found to be 0.285 and 3.91  $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$  from the data reported by Srivastava at 20°.

An alternative analysis of the kinetic data was also made for the sake of comparison on the lines

TABLE 3 — RATE CONSTANTS,  $[\text{Na}^+]$ ,  $[\text{NaS}_2\text{O}_3^-]$ ,  $[\text{NaIOAc}]$  AT VARIOUS CONCENTRATIONS OF REACTANTS FOR  $\text{Na}_2\text{S}_2\text{O}_3$  AND  $\text{IOAcNa}$  REACTION AT 296.16K

| $m$<br>(mol $\text{dm}^{-3}$ ) | $k_{\text{obs}}$<br>( $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$ ) | $[\text{Na}^+]$<br>(mol $\text{dm}^{-3}$ ) | $[\text{NaS}_2\text{O}_3^-] \times 10^3$<br>(mol $\text{dm}^{-3}$ ) | $[\text{NaIOAc}] \times 10^3$<br>(mol $\text{dm}^{-3}$ ) | $I$      | $f(I)$  |
|--------------------------------|---|--|---|--|----------|---------|
| 0.0010                         | 0.454   | 0.002982                                   | 0.00866   | 0.00944  | 0.003973 | 0.05810 |
| 0.0015                         | 0.487   | 0.004461                                   | 0.01833   | 0.02054  | 0.005943 | 0.06979 |
| 0.0020                         | 0.520   | 0.005934                                   | 0.03098   | 0.03546  | 0.007903 | 0.07927 |
| 0.0025                         | 0.540   | 0.007400                                   | 0.04638   | 0.05403  | 0.009853 | 0.08734 |
| 0.0030                         | 0.563   | 0.008860                                   | 0.06426   | 0.07605  | 0.011795 | 0.09443 |
| 0.0035                         | 0.583   | 0.010314                                   | 0.08449   | 0.10140  | 0.013730 | 0.10077 |
| 0.0040                         | 0.605   | 0.011763                                   | 0.10692   | 0.12992  | 0.015656 | 0.10651 |
| 0.0045                         | 0.622   | 0.013207                                   | 0.13140   | 0.16151  | 0.017576 | 0.11178 |
| 0.0050                         | 0.640   | 0.014646                                   | 0.15785   | 0.19605  | 0.019488 | 0.11665 |
| 0.00625                        | 0.680   | 0.018223                                   | 0.23206   | 0.29486  | 0.024241 | 0.12745 |

SRIVASTAVA DATA AT 20°  $K_1 = 2.481$  &  $K_2 = 3.704 \text{ dm}^3 \text{mol}^{-1}$

|          |       |          |         |         |          |          |
|----------|-------|----------|---------|---------|----------|----------|
| 0.000625 | 0.357 | 0.001869 | 0.00346 | 0.00259 | 0.002491 | 0.04679  |
| 0.00125  | 0.384 | 0.003728 | 0.01267 | 0.00988 | 0.004965 | 0.06433  |
| 0.00200  | 0.425 | 0.005946 | 0.03001 | 0.02424 | 0.007916 | 0.007927 |
| 0.00250  | 0.443 | 0.007418 | 0.04493 | 0.03700 | 0.009873 | 0.08742  |
| 0.00500  | 0.500 | 0.014711 | 0.15343 | 0.13536 | 0.019558 | 0.11682  |

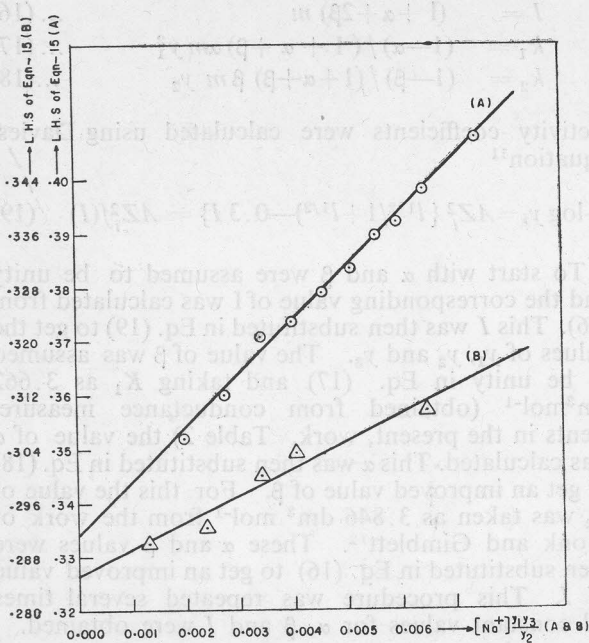


Fig. 2— Plot of L. H. S. of Eq. (15) versus  $[Na^+] y_1 y_3 / y_3$

adopted by Davies<sup>13</sup> for the reaction between  $BrOAc^-$  and  $S_2O_3^{2-}$ . At different ionic strengths, the velocity due to free ions ( $v_1$ ) was subtracted from the total velocity ( $v$ ). Then the residue, i.e. rate with ion-pairs ( $v_1'$ ) should obey the equation

$$-\log \{ [Na^+] [S_2O_3^{2-}] [IOAc^-] / v' \} = \log k_{ip}^0 - 1.018 f(I) \quad \dots(20)$$

The initial velocity of the simple reaction,  $v_1$ , was calculated from Eq. (21)

$$\log v_1 = \log k_1^0 [S_2O_3^{2-}] [IOAc^-] + 2.036 f(I) \quad (21)$$

By subtracting this from the measured velocity, the contribution due to the ion-pairs,  $v_1'$  and hence

$k_{ip}^0 y_1^2$  were obtained. Then the l. h. s. of Eq. (20) was plotted against  $f(I)$  (Fig. 1C) and from the intercept  $k_{ip}^0$  was obtained to be  $9.85 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$  in good agreement with the value of  $9.93 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$  obtained by the previous analysis.

The percentage contributions of ion-pairs reaction to the overall reaction was calculated from Eq. (22)

$$\% \text{contribution of the ion-pair reaction} = 100 (v - v_1) / v \quad \dots(22)$$

The values so calculated were found to be 12.1 at  $25^\circ$  and 4.63 at  $20^\circ$ . This could be due to the ion-association being more at higher temperatures. This receives support from the data in Table 2 ( $K_A$  values are higher at  $25^\circ$  than those at  $20^\circ$ ).

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